

MILORAD DUDUKOVIĆ

Chemical Reaction Engineering
Laboratory (CREL), Department
of Energy, Environmental and
Chemical Engineering, #1
Brookings Drive, Campus Box
1198, Washington University in
St. Louis, Missouri 63130, USA

PAPER

66.023+66.01.001.6:504.06

CHEMICAL REACTION ENGINEERING, ENVIRONMENTAL PROTECTION AND SUSTAINABLE DEVELOPMENT

This paper is based on the lecture delivered at the First South East European Congress of Chemical Engineering (SEECHE1) held on September 25–28, 2005 in Beograd, Serbia. Time constraints did not permit me to publish it in the proceedings of the conference, and since the topic considered is very much pertinent to the current developments in our profession, it seems appropriate to present it in this special issue of the same journal that carried the papers from that conference. In addition, the paper represents a small tribute to my brother Aleksandar for his dedicated work in emphasizing the importance of fundamentals in chemical engineering education. In this paper an attempt is made to illustrate to the younger generations of chemical and process engineers the importance of reaction engineering and its relevance to societal needs globally. The slides and comments of the talk given at SEECHE1 are made available on a web site indicated at the end of the paper.

Key words: Multiphase reactors, Benign processing, Scale-up, Novel technology

It was a special privilege to deliver a lecture on which this paper is based in the large auditorium of Tehnoski Fakultet of the University of Belgrade, where I attended many courses as an undergraduate, in the very hall where my bother Aleksandar ? Sasha mesmerized students with his exciting lectures on transport phenomena and reactions. Since this lecture was well received at the Conference, and the topic is still very much current, this paper will provide the opportunity to those who did not hear it to be exposed to the important challenges that our discipline faces. I will try to provide convincing evidence as to why chemical reaction engineering (CRE), which is at the heart of the chemical engineering discipline, is so important and why it will remain essential in dealing with environmental protection and development of more sustainable process technologies. At the same time I also outline the political challenges that need to be considered in implementation of innovative technological solutions.

Without any doubt today the main challenges confronting mankind, besides improved healthcare, are energy supply, environmental protection and sustainable technologies. The two key factors that affect the environment and sustainability of our industrial practices is the total number of people and their life style. Agricultural methods such as clearing of forest for arable land, irrigation of deserts, the extent of use of herbicides and pesticides, etc., obviously have an important effect on the environment. Mining for finite mineral or energy resources, strip, deep shaft, etc., also affect the

environment. Efficiency of energy utilization, drilling for oil in pristine areas and oceans, use of hydroelectric power, etc., has profound environmental impacts. The types of recreational activity in which we engage, such as cross-country skiing as opposed to driving a snow mobile, walking versus using a dune buggy, have different environmental consequences. How and where we build our dwellings and cities affects the environment. As important as all of the above are, it is *the manufacture of all types of products such as fuels, chemicals, plastics, herbicides, pesticides, medicines and drugs, food additives, etc.* that make alternate life styles possible. It is chemical engineering that deals with the chemical and physical transformation of non-renewable and renewable resources, and intermediates derived thereof, into a variety of useful products to which advanced technological societies in the so called developed world are absolutely addicted. Thus, we chemical engineers, being enablers of this global addiction to our products, have the responsibility to practice it while minimizing the damage to the environment. 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 and damage to the environment. Both the degradation of the environment via pollution 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 [1–5]. The challenges that must be overcome are not just technical but also economical and political in character [6].

Author address: Chemical Reaction Engineering Laboratory (CREL), Department of Energy, Environmental and Chemical Engineering, #1 Brookings Drive, Campus Box 1198, Washington University in St. Louis, Missouri 63130, USA
E-mail: dudu@wustl.edu
Paper received:
Paper accepted:

Process engineers have always been aware of the "11th commandment" which states that "your process should be profitable", so that the recently added "12th commandment" which states "do not pollute" is much easier to implement if to do otherwise leads to dire economic consequences and violation of the 11th commandment! In other words, government regulations and peer pressure of the consumers are conducive to make environmentally benign processes more economically attractive. Technical solutions alone cannot always accomplish that in the current regulatory climate. Moreover, in assessing the environmental impact of our processes and/or products we should include the life cycle analysis of the product to fully understand the environmental consequences of making them and using them [4].

Let us take a brief look as to the global damage to the environment created by our global technological activities in producing the variety of products for the market. The total pollution generated can be, in the first approximation, expressed as a product of three factors: consumption per capita, total population and process inefficiency (= 1 – process efficiency). Both global population and consumption of goods per capita are rising fast. In contrast, process efficiency increases only asymptotically to unity, and these additional increases in process efficiency require ever larger considerable investment of capital and development time. Thus, it seems self-evident that overall pollution (*i.e.* overall damage to the environment) can be most effectively reduced by controlling population growth, and/or by reducing consumption per capita. This engineering logical point of view does not consider the realities of the existing religious and political constraints. The first approach, control of the population, is anathema to two major religions and is 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 envision even the developing world consuming per capita as much as we do in the US! Therefore, the only remaining viable approach left is to seek salvation via improved technology at higher mass, atom and energy efficiency. Thus, as scientists and engineers we must work on dramatic reductions in process inefficiency via improvements of existing and by introduction of novel processes. This, of course, as already stated, requires capital investment and time. As voters we should seek mandatory increases in process efficiencies globally as this seems to be the only viable answer to long term environmental protection.

The US public demanded the change in industrial environmental practices already in the 1980's and this "green wave" has spread through the developed countries of the world. Let us discuss the four methods considered and applied in process industry in order of needed capital expenditures for their implementation [1]. 1) Better house-keeping attempts to eliminate obvious

wastes in the plants and definitely pays for itself while requiring minimal capital expenditures. 2) End-of-the-pipe clean-up usually is the response to public pressure or government regulations. It is only done under regulatory pressure or peer pressure and requires new capital. This method while reducing the environmental damage locally does not improve the various efficiencies of the existing manufacturing process unless it is coupled with recycle of valuable materials or energy recovery. 3) Retrofitting of existing processes introduces better process efficiency and thus reduces waste and pollution and usually leads to energy recovery or recycle of material but it often requires substantial capital expenditures. Economic reasons sometimes dictate plant closure rather than investment in retrofitting. 4) Finally, it is the new technologies and novel processes that offer the best hope for minimization and prevention of pollution but require the largest capital expenditure. The developments in the US demonstrate 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 the company has to be more environmentally responsible to stay in the business due to regulations, or in order to prevent even more dramatic regulations. Changing markets sometime provide the incentive for retrofitting as there is value to be extracted from recycling. New technology does offer expansion and potential dominance of the market and increased profits but is considered only if potential gains are substantial. 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 repeating 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 to its implementation and no instant rewards. However, eventually we will have to embrace the new efficient process technologies due to 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. Use of the current inefficient technologies cannot accomplish this improvement in the living standards of the poor nations without disastrous consequences for the environment since it is too wasteful of materials and energy.

In summary, while serious political and economic barriers exist at present to implementation of environmentally beneficial technologies, on the long run innovative technical solutions will be implemented leading to vastly improved highly efficient technologies.

This development will require many chemical engineers well educated and trained in the science and art of reaction engineering.

THE IMPORTANCE AND ROLE OF REACTION ENGINEERING

Let us now consider why is chemical reaction engineering (CRE) so important. Chemical changes occur in the reactor and their outcome affects profoundly the number, type and size of separation equipment needed after the reactor. The CRE methodology provides a scientific basis for quantifying the 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 [7,8]. An appropriate model of the reactor is multi-scale in character and describes a wide range of length and temporal scales. The molecular scale events determine the mechanism and kinetic rates [9]. 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 local 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. Three basic functions are performed by reaction engineering: 1) determination of key kinetic parameters and selection of appropriate reactor type; 2) scale-up of bench scale information and plant reactor design; 3) troubleshooting of existing reactors. All require a combined experimental and modeling effort. Clearly, performing the first two tasks thoroughly reduces the need for the third one!

From the environmental standpoint, once a potential new product is identified, a search for feasible starting raw materials and reaction pathways for making the desired product at high yield should be conducted [10]. This search should consider all principles of green chemistry in comparing comparative advantages of different reaction pathways and different raw materials. In addition, the life cycle analysis of the product should be attempted [4]. Once a desirable pathway of high atom and mass efficiency is identified, the choice of the reactor type to be used affects the number of separation units needed upstream and downstream and has a profound environmental and economic impact on the

whole process. It has been noted that industries that practice CRE at the high level control wastefulness better than those who are using an ad-hoc approach to reactor selection and design. Let us now briefly discuss the relevance of the three basic reaction engineering tasks mentioned above to environmental protection and sustainability.

1. Reactor Type Selection

To illustrate the pivotal role of reactor type selection 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 carbon disulfide (CS₂). Please, note that atom efficiency of this reaction is 100% as all atoms from each reactant end up in the desired product. So the process is from the atom efficiency point of view preferable to producing CS₂ from methane and sulfur, as was and is the practice in the US and other parts of the world! The refractory lined reactor operated essentially at atmospheric pressure and our task seemed very simple – to replicate the design of the existing kilns and have more kilns constructed in order to increase the plant capacity. As we inspected the kilns in operation we soon discovered that the existing manhole with a heavy cover was not used exclusively for cleaning purposes during shutdowns, as we originally surmised. 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 process gases which in presence of oxygen created a very unhealthy and toxic mix. As a young engineer on assignment to the plant you could not run for cover when these volcanic like eruptions happened because you would have lost the respect of the plant operators whose help you needed in your tasks. So you had to sort of look over your shoulder and nonchalantly say "There it blows again!" This environmentally unfriendly reactor had very dire health consequences for the operators who were exposed to this on a continuous basis since each kiln erupted about once a week and there were about 5 of them!

The point is that the reactor was selected poorly for the process. It was the wrong reactor type. Nevertheless, when we suggested that a fluidized bed reactor with pre-volatilized sulfur feed would not have a hot spot problem and would be stable and work reliably, our suggestion for implementation of a new reactor type was dismissed as too risky. The aversion towards the risk of adopting a new technology (not to replace but even to expand the plant capacity!) led to the decision

that we improve on the existing kilns. We re-designed the hot zone the best we could, only to achieve reduced frequency of blowouts of the new kilns compared to the old ones. That was considered and advertised as a great success by our management (they achieved their goal of increased capacity).

The main point of the above anecdote is that the main attitude towards adopting novel reactor types has not changed in the last 40 years. The management attitude described above prevails in the US and other developed countries as well as in the developing world. As long as one can run a profitable process using old, less efficient technology, one will do it, unless there are regulations in place to prevent fugitive emissions. As long as one makes a profit while using inefficient technology, one is unlikely to accept any risk involved in implementing better technology even when expanding plant capacity or building a new plant at a new location. This type of attitude has led to closures of plants in the developed world, because of increased costs of labor or of meeting more stringent environmental regulations. New plants using the same old technology are then built in the developing world where labor is cheaper and environmental regulations less stringent. Clearly, uniformity of regulations globally would provide a major incentive for introduction of novel technologies. This is particularly important since the challenges in using coal and biomass on a grand scale in producing energy carriers, and the necessity for more efficient large scale technologies in minerals processing, will demand new solutions and more systematic and thorough reactor selection. The basic notions used in selection of reactor type for given reaction pathway are covered in basic reaction engineering texts (e.g. Levenspiel [2]) while the methodology is described in full by Krishna and Sie [11].

The task of getting kinetic data in various reaction systems is also treated in all reaction engineering texts [12], and I will not discuss it here. However, one should point out that the vast majority of the industrial reaction systems are multiphase in character [12,13].

2. Multiphase Reactors: Scale-up and Design

We need to recognize that multiphase reactors are important in all process industries and are involved in production of minerals, bulk and specialty chemicals, petrochemicals, pharmaceuticals, polymers as well as in biomass conversion, energy production and environmental remediation. More than one phase is present in more than 95% of the cases and such systems may involve gas – liquid, gas – solid, liquid – solid, gas – liquid – solid or other multiple phase combinations. In all of these applications it is the chemical reactor, in which chemical transformation takes place that is at the heart of the process. We certainly have to relate and model to some extent the inter-phase and intra-phase transport interaction with kinetics of our

chosen reaction system in the process of arriving at our selection of reactor type, as mentioned earlier. At certain point in process development we face the task of utilizing the performance data obtained on a bench scale reactor of a chosen type in sizing and designing the reactor for the plant. [14,15,16] This is done by either adopting scale-up in parallel or using a vertical scale-up strategy. Scale up in parallel, used routinely for wall cooled tubular packed catalytic reactors, replicates the bench scale unit exactly in numbers necessary to meet plant capacity demands. Reproducing reactor performance requires matching the mean residence time and its dimensionless variance in the laboratory and plant reactor. This is accomplished by using identical tubes for the plant reactor which are packed in the same manner as the bench scale one. Scale-up success is assured provided the flow is perfectly evenly distributed and each tube contains the same amount of catalyst. Reactors with up to 50,000 tubes are not uncommon. Scale-up in parallel is also used in micro-reactors and this ease of scale-up is partly responsible to their great popularity [17,18,19]. However, when the micro-reactor or packed tube concept is not viable, one must engage in vertical scale-up and predict, based on the available bench scale reactor performance, the size and operating conditions for the large scale unit needed to match that performance. This requires knowledge of phase holdups and phase contacting as function of scale and operating conditions. Now for quantitative description of reactor performance it is important to properly describe how are reactants brought into intimate contact 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. We usually rely on ideal reactor assumptions of treating each phase as being either in plug flow or perfectly mixed. When reality does not conform to these assumptions the axial dispersion model is often used to match experimental observations but this approach almost always lacks predictability for scale-up and design. Hence, a new approach is needed.

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 [12,13]. We need a better description via phenomenological models that capture the physics of the flow. We need such models to be based on computational fluid dynamics (CFD) calculations which are experimentally validated at least at some meaningful scale of the equipment. 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 in providing data for such validation 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 [20–22]. Thus, the modern approach to multiphase reactor modeling for scale-up purposes requires: a) capturing the physics of flow by experimental means, b) using CFD models and validating the results experimentally via cold flow experiments, c) developing physically based engineering models for flow and mixing based on the results obtained.

The promise and success of this new approach to multiphase reactor scale-up has been illustrated for numerous reactor types like bubble columns, risers, fluidized beds and stirred tanks. Here, I briefly mention three environmentally relevant endeavors in solid acid alkylations, fuels production from synthesis gas, and biomass production via photosynthesis.

Liquid – Solid Riser. Alkylation is a well established process for production of enhanced high octane fuels (e.g. synthesis of three methyl pentane from butane and butane) and in synthesis of alkyl benzene for detergent applications. The original well established processes use stirred tanks (mixer settlers with heat exchanger) or bubble columns with HF or sulfuric acid as catalyst. The use of these strong mineral acids is undesirable as it creates possible dangerous fugitive emissions and hazardous wastes for disposal. Nevertheless these technologies are currently being licensed throughout the developing world. A quantum jump in technology, and its environmental friendliness, is offered with the invention of super-acid catalyst that can be contained on porous solid support, and with solid acid catalyst deposited on solid support. These catalysts however do deactivate rather rapidly on stream and new reactor configurations suitable to deal with deactivating solid catalyst are required. We considered among different alternatives the liquid–solid riser arrangement [23–26]. It became apparent that a reliable reactor model needed for scale-up can only be developed 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.

By building a prototype cold flow model of the riser, we executed the 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 [24,26]. Liquid tracer studies (with KCl as tracer and electro conductance probes) quickly revealed that liquid is essentially in plug flow (e.g. with the number of tanks in series representing the observed impulse response exceeding twenty, $N > 20$). At the time of our study 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 provided inadequate information for precise design and would have led to incorrect sizing of the riser for a

desired performance. Our Computer Aided Radioactive Particle Tracking Facility (CARPT) was then used to obtain full information about solids flow and mixing pattern [23,25]. An array of twenty eight 2" NaI detectors was employed to monitor 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. 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 from the differences of instantaneous and mean velocities. Gamma ray computer tomography, with a single Cs 137 source and a fan beam of NaI detectors that rotate 360° around the riser, yields the density distribution in horizontal planes at desired elevations. 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 [26]. 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 swirl pattern. Time averaging, however, confirms ensemble averaged 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 allows calculation of eddy 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. As a bonus from CARPT runs in the riser we obtain the residence time distributions of solids which clearly show that solids are much more back-mixed than liquid [26]. 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 of the two phases well. 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 scale-up.

However, we should not forget that we always need to consider the phenomena on all scales. Dramatic reduction in deactivation rate is needed before riser or any other reactor choice can offer advantages significant enough to commercially replace the liquid catalyzed alkylations with solid acid catalysis. Hence, more detailed studies of transport and reaction in zeolites and other solid acid catalysts are needed to answer that question.

Gas-Solid Riser. Gas-solid risers have been used extensively in fluid catalytic cracking and coal combustion with sulfur removal, but here we address the riser application in a novel partial oxidation technology. Butane oxidation to maleic anhydride, with 100% carbon atom efficiency, was introduced and celebrated as a green process as it replaced the old benzene oxidation route. Studies of the vanadium based catalyst revealed an intriguing mechanism involving variable catalyst oxidation states. It became apparent that the old packed bed technology does not exploit fully the advantages of the catalyst and of the new process chemistry, and that one should consider transient operation in order to achieve maximum rates and selectivity. Attrition resistant catalyst was successfully made by proper coating of the vanadium based active core with highly porous but very strong layer. This allowed the use of the circulating fluidized bed (CFB) concept as the ideal reactor configuration to conduct the oxidation of the hydrocarbon feed with the oxidized catalyst in the riser and re-oxidize the catalyst in the fluid bed regenerator. This chemistry at high yield was demonstrated successfully on bench and modest pilot scale size in 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 (riser in this case) and its changes with scale up. Catalyst inventory divided by its recirculation rate, as well as the dimensionless variance of catalyst residence times in the riser and the regenerator, must be kept constant with scale-up. However, in the systems with closed recirculation of solids it is difficult to assess the solids recirculation rate and solids residence time distribution (RTD) in various sections of the CFB system. It is known that impulse injection of tracer leads to non-unique results for solids recirculation rate and solids RTD. Since it became apparent that even after over 50 years of use of CFBs in FCC applications the flow field of solids are not well understood or quantified, a remedy was sought via a cooperative research effort on Multiphase Fluid Dynamics Consortium (MFDRC) funded by the department of Energy (DOE). Our role was to provide reliable data for validation of CFD codes by our

CARPT-CT techniques [27-29]. The experimental facility consisted of a 6" (15 cm) diameter 26 ft (790 cm) tall riser. By tomography we establish that the solid holdup in the down-comer was uniform and by the time of flight measurement of our radioactive particle in the down-comer we assessed exactly the solids circulation rate at different operating conditions. Moreover, by strategically locating detectors at the entrance and exit of the riser we obtained the solids RTD and back-mixing parameters. By recording 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 were able to determine the total time that the tracer particle spends in the riser. We were also able, in addition to the residence time distribution of the particles in the riser, to obtain the first passage time distribution. Such information is not available by conventional tracer studies where a response to a pulse injection of multiple tracer particles is monitored. Significant back-mixing of the solids even in the fully developed flow region over 35 diameters above entry was detected. In the monitored section of fully developed flow a few tracer 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 [27-29]!! 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. This information and the full blown CARPT studies in the riser provide the needed data base for validation of riser models. In turn this should lead to more predictive behavior of riser performance as a reactor.

Bubble Column. Let us look now at the application of CARPT-CT in developing an improved model for many of the bubble column uses [30-35]. In process industry bubble columns are operated at very high superficial velocity to increase their productivity. These are buoyancy dominated churn turbulent flows. We were interested in developing a reliable model for bubble column use in producing fuels from synthesis gas such as in Fischer Tropsch, liquid phase methanol and dimethyl-ether synthesis. We managed to develop a predictive flow pattern model for bubble columns based on CT-CARPT data that were used for validation of CFD codes [35-37]. We have established that in churn turbulent flow an almost parabolic gas holdup profile drives the time averaged global scale liquid re-circulation on which radial and axial eddy diffusivities are superimposed. The model is able with no adjustable parameters, to predict tracer responses to the liquid and gas tracer pulse injection measured at different elevations in an operating pilot plant column at various

processes e.g. liquid phase methanol synthesis, Fischer Tropsch and dimethyl ether synthesis [37]. We have also obtained agreement between Euler – Euler simulations and 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 bubble population balance equation (BPBE) into CFD calculations [38]. It is this level of investigations that is needed to ensure reliable scale up of future reactors for gas conversion to liquid fuels. Examination of the information obtained from the view point of scale-up is still in progress.

DEVELOPMENT OF NOVEL TECHNOLOGIES

The purpose of this short section is to illustrate the importance of multi-scale reaction engineering in development of a new process. Recently algae have received a lot of attention as possible producers of high value added products as well as a potential photo-synthetic route to bio-fuels. The molecular level research focuses on examining the effect of genetic manipulations on yields and rates of synthesis of desired compounds. Reaction engineering focuses on quantifying the effect of varying illumination and ambient conditions on algae growth and strives to establish the most efficient reactor type. Airlift reactors or bubble columns with draft tube, bubble columns with/without a partition (split) and those with an external leg for recirculation are popular in many biological applications. Al Dahhan and Luo [39,40] studied growth of micro algae/cyano bacterial cultures as biomass source for food and feed and as renewable energy source in such reactors. Through the photo synthetic process algae fix carbon dioxide and release oxygen. So availability of light is essential. Cells in their passage through the reactor get exposed to different levels of illumination. Too little light leads to photo limitation; too much light causes photo inhibition. A proper cell level model was established to quantify the effect of light on growth. It was shown that proper mixing can significantly enhance the beneficial flashlight effect [39–41]. Using CARPT the velocity flow pattern of algae in the system consisting of a riser and downer section was established. 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 leads to the prediction of reactor performance of the various reactor types. Upon CFD validation, one can use the combined reactor and cell model to predict cell concentration in various reactor configurations. It was found 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!

This example and the previously discussed concepts illustrate that the systems based multi-scale reaction engineering approach is needed in development of environmentally beneficial engineered systems. We have joined the lead of the University of Kansas, and with them, University of Iowa and Texas A&M Prairie View University entered into a partnership in a Center for Environmentally Beneficial Catalysis. CEBC became a reality as one of the 4 new National Science Foundation (NSF) Engineering Research Centers (ERCs) on September 1, 2003 and is now in its 4th year of existence. The objective of the Center is to implement a highly interactive multiscale approach consisting of experiments and modeling to the development of new environmentally beneficial catalytic processes. Reaction engineering is playing a pivotal role.

SUMMARY AND CONCLUSIONS

In conclusion, the best way to prevent pollution is at the source. This, in addition to selection of green chemistry, requires the application of multi-scale reaction engineering approach, consisting of molecular, particle/eddy and reactor scale considerations, to the analysis of the desired reaction pathways and selection of the best reactor type. Most reaction systems involve multiphase flows and we must validate computational fluid dynamic codes for them before we can use them in design and scale up. 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 suitable for scale-up. The utility of such models in alkylation, partial oxidations, synthesis gas conversion and other applications has been illustrated.

Sustainable technology depends on the selection of appropriate material resources and reaction pathways and on the ability to renew the starting materials by recycle or other means like photo-synthesis. Developing an idea for sustainable environmentally beneficial technology requires considerable research investment not only at the molecular level of inquiry but at all scales involved in the process. Converting an idea for sustainable technology to an actual process requires understanding and application of multi-scale reaction engineering principles. Development of experimental and modeling resources for advancing state of the art descriptions of reactor scale flow patterns and mixing demands significant resources. Implementation of new environmentally beneficial technology often must overcome economic and political barriers and could be helped by globalization of the regulatory environment and by proper tax incentives. Reactor scale research must be pursued on par with molecular scale discoveries since reactor scale advances are needed in addition to molecular scale discoveries to convert green chemistry to green engineering and sustainable processes.

ACKNOWLEDGEMENT

The author is 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.

Note: The lecture based on which this paper is written, slides and notes is available on the web.

REFERENCES

- [1] Chemical Manufacturers Association. Preventing pollution in the chemical industry. 1982-1990, CNA, Washington D.C. 1992.
- [2] H. DeLasa, G. Dogu, A. Ravella, NATO ASI Series E., Vol. 225, Kluwer Acad. Publ. 1992.
- [3] M.P. Dudukovic, P.L. Mills, I&EC Res. **33** (1999) 2885-3069.
- [4] T.D. Allen, D.T. Shonnard, Green Engineering: Environmentally conscious design of chemical processes, Prentice Hall, 2002, p. 552.
- [5] C. Tunca, P.A. Ramachandran, M.P. Dudukovic, Role of chemical reaction engineering in sustainable engineering principles, in Elsevier, M.A. Abraham (editor), 2007, in press.
- [6] B.H. Huesemann, B.H. Clean Techn. Enviro. Policy. **5** (2003) 21-34.
- [7] H. Kramers, K.R. Westerterp, Elements of chemical reactor design and operations, Acad. Press, NY, 1964.
- [8] O. Levenspiel, Chemical reaction engineering, J. Wiley, NY, 1962.
- [9] J.J. Lerou, K.M. Ng, Chem. Eng. Sci. **51** (1996) 1595-1614.
- [10] J.M. Douglas, I&EC Research. **31** (1992) 238-243.
- [11] R. Krishna, S.T. Sie, Chem. Eng. Science. **49** (1994) 4067-4084.
- [12] M.P. Dudukovic, F. Larachi, P.L. Mills, Chem. Eng. Sci. **54** (1999) 1975-1995.
- [13] M.P. Dudukovic, F. Larachi, P.L. Mills, Catalysis Reviews - Science and Engineering. **14** (2002) 123-246.
- [14] A. Bisio, R.L. Kabel, Scale-up of chemical processes, J. Wiley, N.Y., 1985.
- [15] J.P. Euzen, P. Trambouze, J.P. Wauquier, Scale-up methodology for chemical processes, Technip Paris, 1993.
- [16] P. Trambouze, J.P. Euzen, Chemical reactors - from design to operation, Techip, Paris, 2004.
- [17] K.F. Jensen, Chem. Eng. Sci. **56** (2001) 293-306.
- [18] H. Lowe, W. Ehrfeld, Electrochem. Acta. **44** (1999) 3674-3685.
- [19] V. Hessel, P. Angeli, A. Gavrilidis, H. Loewe, I&EC Research. **44** (2005) 9750-9769.
- [20] J. Chaouki, F. Larachi, M.P. Dudukovic, (editors), Non-Invasive Monitoring of Multiphase Flows, Elsevier, 1997a.
- [21] J. Chaouki, F. Larachi, M.P. Dudukovic, Ind. Eng. Chem. Res. **36** (1997b) 4476-4503.
- [22] M.P. Dudukovic, Oil & Gas Science and Technology. **55** (2000) 135-158.
- [23] S. Roy, J. Chen, S.B. Kumar, M.H. Al-Dahhan, M.P. Dudukovic, Ind. Eng. Chem. Research. **36** (1997) 4666-4669.
- [24] S. Roy, M.P. Dudukovic, Ind. Eng. Chem. Res. **40** (2001) 5440-5454.
- [25] S. Roy, A. Kemoun, M.H. Al-Dahhan, M.P. Dudukovic, AIChE J. **51** (2005) 802-835.
- [26] S. Roy, Phase distribution and performance studies of gas-liquid monolith reactor, D.Sc. Thesis, Washington University, St. Louis, 2000.
- [27] S. Bhusarapu, Solids flow mapping in gas-solid risers, D.Sc. Thesis, Washington University, St. Louis, 2005.
- [28] S. Bhusarapu, M.H. Al-Dahhan, M.P. Dudukovic, Chem. Eng. Sci. **59** (2004a) 5381-5386.
- [29] S. Bhusarapu, M.H. Al-Dahhan, M.P. Dudukovic, Powder Tech. **163** (2006) 98-123.
- [30] S.B. Kumar, D. Moslemian, M.P. Dudukovic, AIChE J. **43** (1997) 1414-1425.
- [31] N. Devanathan, D. Moslemian, M.P. Dudukovic, Chem. Eng. Sci., **45** (1990) 2282-2291.
- [32] M.P. Dudukovic, S. Degaleesan, P. Gupta, S.B. Kumar, ASME Proceedings, FEDSM '97, 1-5, June 22-26, 1997, p. 3517.
- [33] S. Degaleesan, M.P. Dudukovic, Y. Pan, AIChE J. **47** (2001) 1913-1931.
- [34] P. Gupta, B.C. Ong, M.H. Al-Dahhan, M.P. Dudukovic, B.A. Toseland, Catalysis Today. **64** (2001a) 253-269.
- [35] S. Degaleesan, M.P. Dudukovic, B.A. Toseland, B.L. Bhatt, Ind. Eng. Chem. Res. **36** (1997) 4670-4680.
- [36] P. Gupta, M.H. Al-Dahhan, M.P. Dudukovic, B.A. Toseland, Chem. Eng. Sci. **56** (2001b) 1117-1125.
- [37] P. Chen, P. Gupta, M.P. Dudukovic, B.A. Toseland, Chem. Eng. Sci. **61** (2006) 6555-6570.
- [38] P. Chen, J. Sanyal, M.P. Dudukovic, Chem. Eng. Sci. **60** (2005) 1085-1101.
- [39] H-P Luo, A. Kemoun, M. Al-Dahhan, S.J.M. Fernandez, S.J.C. Garcia, G.E. Molina, Chem. Eng. Sci., **58** (2003) 2519-2527.
- [40] H-P Luo, M.H. Al-Dahhan, Biotech. & Bioeng. **85** (2004) 382-292.
- [41] H-P Luo, Analyzing modeling of airlift photobioreactors, D.Sc. Thesis, Washington University, St. Louis, 2005.