PART I

Hello everyone and welcome to your first audio lecture to the course “Chemical and biological reaction engineering”. My name is Dr. Mwikali and for the next ten to twenty minutes we are going to dig deeper into the course work and have a great understanding of the practical applicability of all the processes involved in this branch of engineering. All the audio lectures will be between 10 and 20 minutes as I had said earlier. The lectures in scripts may not match the audio lessons as I may not express the mathematical expressions well in audio but what I will not express clearly, will be in the scripts. We will cover a lot of ground application of chemical and biological reaction engineering to our requirements in chem/ bio process industry and as well as in daily life and so on. The objective here is to try and bring to your attention the main purpose of this course and then what is the methodology that we will follow; and how we plan to address various issues; and how we will explain the principles through various examples and so on. So, the methodology we will try to drop here is one of problem solving and we learn how to derive the equations that describe certain process and or certain idealization that we look at and also show how it implies to different situations.

I hope you are all prepared. So, let’s get started.

LECTURE 1

Abstract

The importance of reaction engineering in generating a myriad of products on which developed societies depend is outlined. The challenges of a political, economic, and technical nature that need to be addressed in rendering conversion of raw materials into desired products that are more environmentally friendly and sustainable are briefly discussed. It is shown that multiphase reactors are prevalent in all applications, and improvements in the reactor material and energy efficiencies lead to more environmentally benign processes. This requires, in addition to the selection of green process chemistry, systematic implementation of the multi-scale reaction engineering methodology to accomplish proper reactor type selection and scaleup for commercial applications. It is also illustrated that recent innovations in multiphase reaction engineering basically utilize two key concepts: process intensification (for example enhancement in mass and heat transfer rates) and simultaneous reaction and separation. Examples of these are discussed, such as micro-reactors, reactive distillation and so on and so forth. It is also shown that commercialization of bench-scale discoveries requires either scaleup in parallel or vertical scaleup. New tools for visualization of opaque multiphase flows and development of appropriate rational phenomenological multiphase reactor models for scaleup and design are also briefly discussed.

Introduction

This lecture will summarize the key roles of the challenges that face the process industry today and in generating needed innovations. The argument is made that only improved understanding and development of the rational basis for scaleup and design of multiphase processes will ultimately bring us to improved atom, mass, and energy efficiencies needed for sustainable processes of the future. However, the ultimate commercial implementation of these technical innovations in novel technologies will depend as well on political and economic factors.

Without question, in the process industry our key challenge is in devising sustainable and more efficient processes for the future. We must generate energy carriers and fuels in a more efficient and in an environmentally acceptable manner, and we must produce various products at improved material and energy efficiency while increasingly switching to the use of renewable resources. That presents tremendous opportunities for innovations. While creative new ideas can be nurtured, their transformation to innovative processes requires systematic application of reaction engineering principles and overcoming political and economic barriers.

The domain of chemical engineering consists of physical and chemical transformations (and that includes biological) of starting materials derived from nonrenewable and renewable resources into a variety of products for the market on which we depend to support our life-style. The key to economical, environmentally friendly, and energy-efficient processes is in choosing the right chemical transformation, the right catalyst for it, and the right reactor type and being able to scale up these transformations for commercial use and public benefit. While the reactor by itself typically does not represent the major capital or operating expenditure in a process, the type of reactor used and its mode of operation determine the needed number and size of separation units in the process train and ultimately affect the cost of the whole process. Thus, choosing the right reactor and operating it properly is essential for the success of the process. That success has been traditionally measured in terms of profitability achieved. Recently, metrics of quality increasingly include measures of environmental impact, thus providing the incentive for implementation of environmentally benign and sustainable processes. This change has occurred due to the realization that our processes create globally a tremendous impact on the environment. For example, in the first approximation, total global pollution generated is a product of consumption per capita, population, and process inefficiency (= 1 − process efficiency). It seems self-evident that pollution can be reduced directly by controlling population growth and/or by reducing consumption per capita. In contrast, process efficiency increases only asymptotically to unity and requires considerable investment of capital and time. Moreover, improving the efficiency of one process unit may lead to inefficiency elsewhere. Nevertheless, neither population control nor reduction in consumption per capita is politically acceptable, leaving us only with innovations in process technology and increased process efficiencies as plausible solutions in seeking sustainability and global pollution reduction. Hence, a holistic systems approach and life cycle analysis are needed in new process and product development.

The desire to become “greener” in processing has always been tied to the requirement to be profitable. In attempting to reduce the damage to the environment by the process industry during the past 15-plus years in the world we have focused on the following activities: Better education of personnel at existing manufacturing facilities has resulted in better operating practices and paid for itself. Retrofitting of existing facilities was done whenever it was clear that it will result in improved profitability (otherwise offending facilities were closed). Installation of end-of-the-pipe cleanup equipment was pursued when required by law or peer pressure, provided processing remained economical. Moving and opening facilities offshore was often practiced to increase profitability. Unfortunately, this almost always resulted in licensing of old (post-World War II technology) at locations with more favorable regulatory climate, lower labor costs, or cheaper access to raw materials. Instead, what we need is the development and installation of new cleaner and more efficient technologies. This requires *innovation*. It also requires substantial capital expenditures and is perceived as involving considerable risk. Clearly, by investing more in the science of scaleup such risk will be reduced and the willingness to implement new technology will increase. This is the challenge for multiphase reaction engineering in the next few decades.

In summary, globalization of environmental regulations and adoption of global progressive tax policies that would encourage and reward process innovations resulting in improved process efficiencies, in reduced environmental impact, and in favorable product life cycle analysis would go a long way in ensuring the development of more sustainable technologies. Then, the remaining issues would be of only a technical nature and could be handled by advancing the reactor engineering and process development methodologies.

Multiphase Reaction Engineering

The transformations involved in conversion of raw materials to products invariably involve multiphase reactor technology in all industrial sectors (e.g., energy, liquid fuels, syngas and natural gas conversion; bulk chemicals, fine chemicals, and pharmaceuticals production; biomass conversion; petroleum refining; polymer manufacture; production of materials such as semiconductors and optical fibers; environmental remediation).

PART II

These activities generate a large contribution to the gross domestic product (GDP) of countries such as the United States. **Chemical reaction engineering** (CRE) methodology, developed over the past 60 years, offers a rational way to quantify reactor performance based on application of mass, energy, and momentum balances to the multi-scale transport and kinetic interactions. Thus, we attempt to quantify the rates of events on the molecular scale, i.e., the kinetic rates of molecular interactions at prescribed temperature and composition conditions unhindered by transport effects, the micro intra-phase and interphase transport rates on the scale of a single catalyst particle or a single turbulent eddy, and reactor-scale phase contacting and flow pattern distributions and exchange rates in addition to heat transfer rates. Understanding these multi-scale transport kinetic interactions is the key to the selection of the best reactor type and operating conditions for a given chemistry and to successful scaleup of bench-scale demonstrations of novel molecular scale discoveries to commercial practice. The level of implementation in industrial practice of Chemical reaction engineering CRE methodology in the past depended on the type of industry and production rates. Production of fuels and commodity chemicals required high material and energy efficiency to be competitive and Chemical reaction engineering CRE was implemented at a high level. Specialty chemicals and pharmaceuticals under patent protection for their high value-added products could afford to sacrifice efficiency for the sake of expediency and practiced Chemical reaction engineering CRE at a low level. Remarkably, this is reflected in the environmental impact factor of these industries. Petroleum refining at one extreme has a low environmental impact factor (E-factor) and generates very few unwanted by-products per unit of product produced. The pharmaceutical industry, at the other extreme, creates an enormous amount of waste per product and has a very high environmental impact factor. The E-factor is now gradually changing for the better in all industrial sectors

In the past chemistries for commercial applications were selected based on economic drivers but with very little additional environmental consideration. This is now changing. The principles of green chemistry, environmental impact factor assessment of the process to be implemented, and life cycle analysis of the products to be made should be used prior to embarking on commercialization of new chemistries. The chemistry selected for commercialization should have potentially high atom, material, and energy efficiency. It is then up to the proper selection of reactor type and its operating conditions to ensure that such high efficiencies will be realized in commercial practice. The choice of the proper reactor type and operating conditions for a given process chemistry is the key factor in determining volumetric productivity and selectivity, and it should be based on a rational approach founded on a reactor model. Such a model must capture the events on a multitude of scales at the right level and provide the means to scale up test tube discoveries to commercial processes. The complexity arises from the fact that the interactions of events on various scales are dependent on the scale of the equipment. It is also increasingly necessary, in order to use novel, more active catalysts, to understand the change of the flow pattern with the reactor scale and its interaction with mesoscale and microscale transport. Hence, improving our level of understanding of all scales affecting reactor performance, i.e., becoming more quantitative and predictive, is needed for safer scaleup and design of the next generation of reactors.

It is clear that adopting green manufacturing principles requires technological as well as political changes. On the technical side further improvements in our ability to quantify kinetic transport interactions are needed, and this requires further advances in Chemical reaction engineering CRE methodology

Process Intensification

The systems approach involved in the selection of the most suitable reactor type for a chosen chemistry has been advocated and its advantages have been illustrated in the literature. By examining the chemistry requirements and the molecular, microscale, and reactor-scale transport kinetic interactions it is possible to select the best catalyst particle size, best reactor flow and contacting pattern, and best flow regime in order to optimize the desired objective function that involves volumetric productivity and selectivity. However, instead of considering only classical reactor types one should also examine possible means of process intensification. This can be accomplished by combining reaction and separation in one unit, by designing new reactor configurations or modes of operation, and by miniaturizing the reactor in order to enhance all transport rates. Let us briefly illustrate some of these methods.

In equilibrium-limited reactions conducted in packed bed or tubular reactor—type configurations it is highly advantageous to remove the product in situ. This can be effectively accomplished by reactive or catalytic distillation. A remarkable process innovation involving the reactive distillation concept was commercially implemented by Eastman Chemicals in methyl-acetate synthesis. It replaced a multicolumn integrated process with a single-column design. Capital and operating costs were dramatically reduced. There is a rich literature on catalytic and reactive distillation and several process applications. Nevertheless, a large gap remains between academic analysis and Classification of reactive distillation processes by dimensionless numbers. Steady state multiplicities in an ethylene glycol reactive distillation column clearly established that reactive distillation in ethylene glycol synthesis could produce greatly improved yields of the desired product while feeding water and ethylene oxide in an essentially stoichiometric one-to-one ratio. This avoids massive recycle of organic contaminated water, which is required in conventional technologies that use tubular reactors with 40-to-1 or larger water-to-ethylene oxide ratio. Somehow this possible improved process redesign was never adopted. Since with respect to toluene we have consecutive reactions and with respect to chlorine competitive reactions, reaction engineering teaches us that we need plug flow of toluene as the liquid phase and cross flow that is back-mixed for chlorine. Commercially, to achieve this favorable flow pattern for the formation of the intermediate, the liquid phase flows through a series of bubble columns, with light wells since the reaction is photochemical in nature, while chlorine is fed in parallel and bubbled into each column to keep its concentration low. Thus, the liquid experiences plug flow and gas is close to well mixed at its exit composition in each column. Typical selectivity of 90% can be obtained at toluene conversion of up to 30%. We have shown that by conducting the process in photoreactive distillation mode we can achieve selectivity of better than 96% at toluene conversion well above 90%. This idea can be implemented, in principle, on the microscale or macroscale, but this reaction may be too slow for the microscale. No interest seems to exist to transfer this to commercial scale due to nontechnical factors.

There are other ways of overcoming equilibrium limitations. One is to remove the product in situ via a selective membrane. In situ product separation in butanol fermentation by membrane-assisted extraction by trickling a fine solids adsorbent in a catalyst-packed bed counter currently to the flow of gas. This will be a model for a countercurrent gas-solid-solid trickle flow reactor for equilibrium reactions. The methanol synthesis demonstrated in pilot plant experiments that 100% conversion of syngas to methanol is possible. Commercial applications did not follow for reasons unknown. One can speculate that an attrition-resistant adsorbent could not be developed or that the companies with vested interest in the existing technologies managed to suppress the innovation. Membrane reactors have been advocated for selective product removal as well as for selective addition of a reactant, which can dramatically improve the selectivity in complex reactions. In spite of numerous articles in scientific journals describing potential advantages of such systems and providing laboratory-scale examples, the confidence in membrane technology for large-scale applications seems to be lacking even today. One hopes that this will change in the future.

Yet another way of overcoming equilibrium limitation is by reverse-flow dynamic operation of adiabatic packed beds. In running adiabatic packed beds for exothermic reactions is well known that the temperature rise adversely affects the achievable exit conversion due to equilibrium limitations, since the equilibrium constant goes down with increased temperature. Hence, an idea patented by Cottrell in the 1930s. Purifying gases and apparatus therefor of swinging the bed feed periodically from one side to the other, achieves a more favorable inverted-U temperature profile. This approach was embraced by many in the reverse-flow concept, which was commercially implemented in sulfuric acid manufacture and VOC abatement, for example, The *Catalytic Processes under Unsteady-State Conditions* shows that idea further in our Chemical Reaction Engineering Laboratory by coupling an exothermic reaction (like methane combustion) with an endothermic one (like methane reforming) in periodic operation with feed switching from end to end. Such Modeling shows that there is a region of operability where complete conversion for both reactions and high thermal efficiency can be achieved.

Let us now consider innovations that result from attempts to design a reactor so as to best accommodate the catalyst. It is well known that many catalysts are highly active and selective for very short time. We essentially “kill” them by steady-state operation as at such conditions they exhibit much lower activity and selectivity towards the desired product. There are ways of improving the productivity and selectivity of such catalysts. For example, novel greener chemistry to maleic anhydride starts with butane (instead of benzene), which undergoes partial oxidation with air. This is best done on a vanadium phosphorous oxide (abbreviated VPO) catalyst. To improve vapor phase catalytic oxidation of butane to maleic anhydride, we must give rise to the Activation of vanadium phosphorous oxide catalysts for alkane oxidation. This is the influence of the oxidation state on catalyst selectivity. However, that catalyst is very active and selective only in a specific oxidation state when it donates its active oxygen to the hydrocarbon to produce maleic anhydride via partial oxidation. The old technology, inherited from benzene oxidation, uses a packed-catalyst bed with simultaneous premixed hydrocarbon and air feeds and does not utilize the catalyst to its full potential in steady-state operation. For maximum efficiency the catalyst requires rapid reduction with hydrocarbon and re-oxidation with air. This can readily be accommodated by a circulating fluidized bed arrangement where partial oxidation of HC and reduction of the catalyst occurs in the riser and re-oxidation of the catalyst by air in the fluidized bed regenerator. Special catalyst with a highly porous but attrition-resistant outer surface has been developed and successfully used in numerous oxidation reduction cycles. Nevertheless, scaleup from a pilot plant riser that is four to six inches in diameter to a full-scale plant with a reactor diameter of many feet involves risks due to incomplete knowledge of the dynamics of such gas-solid systems. Innovation needed to reduce such risk is discussed later. At this point one should mention that successful periodic operation has been commercially demonstrated for a number of systems that utilize UOP's pressure swing adsorption-desorption process. The micro reactor concept for multiphase systems has been well established and offers great advantages for very fast and highly energetic reactions. It also offers scaleup advantages, as discussed below.

Scaleup

The key objective of reaction engineering is to transfer molecular-scale discoveries to commercial practice in a rapid, safe, economical, and environmentally acceptable manner. The key scaleup issue is the following: once the reaction system was successfully run in the laboratory and produced the desired conversion, yield, and selectivity, how could the results be reproduced at a commercial scale. Horizontal scaleup (scaleup in parallel or scaleup by multiplication or scale-out) offers one alternative, while vertical scaleup offers another. Only the latter must account for the effect of equipment scale on the interplay of transport and kinetics. The former keeps the geometry, flow and contacting pattern, and flow regime the same but has to deal with the logistics of system integration and flow distribution. Hence, without proper understanding of the system, scaleup and design that rely solely on statistical approaches have a high likelihood of failure. Key scaleup considerations require us to match the mean residence times or mean contact times in multiphase systems. This requires the knowledge of phase holdups and of their actual flow rates through the system. To ensure the same performance we must also match the variance of the residence times in the reaction environment and/or the covariance of sojourn times in different phases. This requirement is often forgotten. Naturally we must also ensure the same heat transfer per unit volume.

Scaleup by multiplication is practiced routinely for wall-cooled tubular and packed bed reactors. Once the satisfactory performance of one tube is accomplished, the number of tubes needed for commercial production is determined. Success depends on availability of reliable single tube data, a good knowledge base for manifold and flow distributor design, and know-how to avoid external heat transfer limitations upon scaleup.

For many decades industrial chemists experimented with a catalytic tube of one to two inches in diameter of desired lengths (like or longer). Once the feed temperature and composition and flow rate used (i.e., mean residence time) produce the desired result, scaleup is simple in principle. It requires using N tubes identical to the one used in the laboratory, packed with the same catalyst particles and receiving the same feed at the same flow rate as the tube in the lab. The number of tubes N needed is given by the ratio of the desired commercial production rate to that achieved in the laboratory. Lurgi and others build reactors with up to 50,000 tubes!

This concept of the ability to scale up in parallel is a great advantage that micro reactors also offer. Let us look now at some of their other advantages such as:

PART III

(1) high surface-to-volume ratios and, due to small dimensions, enhanced mass and heat transfer coefficients by one to two orders of magnitude,

(2) laminar flow conditions and low pressure drop but ability to make residence time distribution (RTD) narrow by introduction of another phase,

(3) controllable RTD and back mixing,

(4) high volumetric productivity,

(5) low manufacturing and operating costs,

(6) increased safety due to small amount of material, and

(7) scaleup in parallel (scale out). The MIT group of Klavs Jensen, among others, has recognized the importance of being able to manipulate multiphase systems in micro reactors and they have shown that one can get competitive performance for various reactions and separations and in material synthesis The achieved performance of the micro reactor depends on the level of understanding of the chemical system and the ability to manipulate micro reactor design so as to meet the reaction contacting requirements best. If the desired figures of merit are met, then scaleup in parallel ensues. Microfluidic synthesis of colloidal silica, in principle, scaled up to large production rates which was possible even for highly exothermic reactions such as direct fluorination of aromatics. Gas/liquid and gas/liquid/solid micro-structured reactors—Contacting principles and applications summarize well the contacting principles in gas-liquid and gas-liquid-solid micro reactors. They review the characteristics of a variety of contacting patterns attempted and report vastly improved mass and heat transfer coefficients, much larger interfacial areas, controllable RTDs, increased volumetric productivity, and ease of scale out. They offer demonstrations of successful bench-scale use in direct fluorinations, oxidations with fluorine, chlorination, sulfonations, and hydrogenations.

Enthused by potential for significant process intensification, a number of companies are involved in R & D for potential commercialization. Micro-reaction engineering: Is small really better? paper presented at CREL (Chemical Reaction Engineering Laboratory) In Annual Meeting, Washington University in St. Louis, October 2005, the following question arose. With all their perceived advantages, and the technologies available to manufacture micro reactors in silicon in glass and in steel or other metals, why aren't they more widely used? The answer is that they require very fast reactions and active stable catalyst (usually these two do not go together). Most importantly, micro reactors are, due to small dimensions, more prone to fouling and clogging and leaks between channels, and their reliability and life on stream is an unknown.

All of these are potentially solvable problems on a case-by-case basis. However, the perceived risk factor is too large for them to replace existing installations. Most likely, acceptance of micro-devices will occur first in consumer products, distributed power systems, highly energetic fast reactions, and in situ production of hazardous chemicals. Other applications will be slower.

Innovations in Vertical Scaleup

In numerous chemistries that involve multiphase reactors the use of micro reactors may be impractical. Thus, vertical scaleup is needed. We briefly address here the novel techniques available to reduce the risk of such vertical scaleup. As example we consider systems with two or more moving phases. It is now important to describe the flow pattern of each phase and assess their dependence on the scale of the equipment. In the past we often relied on ideal reactor flow pattern assumptions of treating each phase as being either in plug flow or perfectly mixed. This, however, is only an approximation of reality and does not allow one to account for differences caused by the changes in equipment scale. Since reality often does not conform to the ideal flow assumptions in the equipment experimentally tested, the axial dispersion model (ADM) is often used to match experimental observations. It has been recognized, however, that axial dispersion model ADM is not predictive. It is difficult to extrapolate the available data for the axial dispersion coefficient of each phase to the plant scale in the absence of sound theory, which is often lacking. One needs more accurate flow and mixing models based on the physical phenomena that occur in the system. Since multiphase systems like these are almost always opaque, it is important to develop means to measure phase holdup and velocity distribution in them. Such data are also essential for validation of computational fluid dynamic (CFD) models that must be used on the reactor scale. Once validated, such CFD models can be used to produce data needed for development of engineering models for coupling with kinetics.

Thus, the modern approach to reactor modeling and scaleup requires:

- Capturing the physics of flow by experimental means,
- Using appropriate CFD models and validating the results experimentally, and
- Completing physically based engineering models for flow and mixing and coupling them with kinetics.

To quantitatively assess phase holdup distribution in multiphase systems most groups involved builds a gamma ray computer tomography (CT) scanner that can provide them with the density distribution at any desired cross section of the reactor. A gamma ray tomographic scanner for imaging void fraction distribution in bubble columns is used to measure the motion of the solids or liquid phase we have introduced computer-assisted single radioactive particle tracking (CARPT) to obtain the Lagrangian trajectories of a single tracer particle made dynamically similar to the phase being traced. For monitoring solids motion a particle of the same density and size as the solids used is employed, for liquids a neutrally buoyant particle is used whenever possible. Tracer particle position in time is detected with frequencies up to 200 Hertz. From the obtained Lagrangian trajectories, the instantaneous velocities are obtained, as well as time average (ensemble average) velocity values, and various statistical properties of the flow (i.e., eddy diffusivities). The techniques and data reduction procedures have been described in detail in a number of publications, including a number of student doctoral theses.

Liquid-solid riser has been considered as a reactor for solid acid catalyzed alkylation in replacing HF and sulfuric acid as catalysts. The key design issue, due to rapid catalyst deactivation, is the flow pattern of liquid and solids in the riser and the extent of back-mixing of the solid catalyst in the riser. Classical impulse response tracer studies confirm that liquid is in plug flow. How about solids? The working design assumption is plug flow of solids or some leakage of solids backwards interpreted by empirical axial dispersion coefficient. Use of CARPT and CT provides the database coupled with the CFD model for an improved model of solids flow and solids back-mixing. Both CFD computations and CARPT tracer particle trajectories reveal a highly complex three-dimensional instantaneous flow structure. Time averaging of CFD calculations and ensemble averaging of CARPT data produces solids velocity profiles in close agreement with each other, with solids on the average rising in the middle of the riser and falling down by the wall. The agreement between simulations and data is great for solids velocity, solids holdup distribution, and granular temperature, i.e., solids kinetic energy.

This now provides us with the proper model for the riser. It consists of plug flow of liquid (proven experimentally by tracer study and indicated by CFD, as liquid RTD can be matched by 20 tanks in series) and of the developed solids axial velocity profile with superimposed axial and radial diffusivities. This model can now be coupled with appropriate reaction and deactivation kinetics. CFD can predict all the flow model parameters. The effect of increase in riser diameter required by scaleup is modest and not an issue.

Gas-solid riser is used in circulating fluidized bed (CFB) technology in many applications, most notably in fluidized catalytic cracking (FCC), fluidized bed coal combustion, and redox systems like the one previously mentioned for butane oxidation to maleic anhydride on VPO catalyst. The key issues are maintenance of the same contact time and of dimensionless variance of the solid’s residence tines in the riser. Mean contact time depends on the solids holdup in the riser and its circulation rate. Neither can be measured directly on a CFB with closed-loop solids circulation except via CARPT/CT. We generated important and unique data for validation of CFD models in various flow regimes in the riser. To match the dimensionless variance of the solids residence time distribution (RTD) in the riser, one must first know what that RTD is. We have shown that only CARPT can provide the correct answers and have examined the RTD in various flow regimes, providing a challenge for CFD modelers to generate results in agreement with data. Once that is accomplished, CFB scaleup can be based on firmer grounds.

Summary and Conclusions

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

In addition to the adoption of green chemistry principles, it is vital to master the scaleup methods based on fundamental reaction engineering principles.

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

Miniaturization provides opportunities for scaleup in parallel, and quantification of multiphase flow fields reduces the risk of vertical scaleup. Both are needed for rational process intensification.