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Trends in catalytic reaction engineering

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Abstract

Catalytic reactions in multiphase systems are prevalent in production of fuels, bulk and specialty chemicals, pharmaceuticals, materials, food and feed, etc. Making useful products, at economical yields and selectivities, from the diverse chemistries in such a broad range of applications requires the ability to quantify the interplay of transport phenomena and kinetics. This is the domain of catalytic reaction engineering. In this paper the current state of the art of this discipline is briefly reviewed with the emphasis on describing the increased use of fundamentals in multiphase reactor modeling and scale-up. Packed beds, trickle beds, slurry bubble columns, simultaneous reaction and separation via catalytic distillation, membrane reactors and trickling solids adsorbent, as well as nonconventional multiphase reactor operations are discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic processing, involving multiphase systems, is wide-spread in the production of fuels (a modern refinery greatly relies on it), commodity chemicals (manufacture of ammonia, methanol, sulfuric acid and all other basic chemicals is heavily dependent on it), specialty chemicals and pharmaceuticals (this area alone accounts for a 60 billion US dollars market in USA). Such processing is equally important in pollution abatement (e.g. NO_x reduction and VOC abatement), and in production of food and feed where both conventional and enzyme catalysis is employed. The success of catalytic processing of multiphase systems has resulted from a synergetic approach to the problem by chemists and chemical engineers. Traditionally, the focus of the chemists has been on the catalyst, its preparation, active form, activity, active centers, turnover numbers, kinetics and poisons that might damage it. Engineers were mainly concerned with how to bring the reactants effectively in contact with the chosen catalyst form, and how to provide or remove the heat associated with the progress of reaction. They also concerned themselves with scale-up issues, as how to repro–duce the selectivity and rates reached in the laboratory on large process scale. Catalytic reaction engineering (CRE) emerged as a powerful methodology that quantifies the interplay between transport phenomena and kinetics on a variety of scales and allows formulation of quantitative models for various measures of reactor performance such as production rate, conversion and selectivity. Our ability to establish such quantitative links between measures of reactor performance and input and operating variables is essential in optimizing the operating

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conditions in manufacturing, for proper reactor selection in design and scale-up, and in correct interpretation of data in research and pilot plant work. A starting point in catalytic reaction engineering is the formulation of a reactor flow model based on which species mass conservation equations and the energy balance can be written as

$$(\text{rate of input}) - (\text{rate of output}) + (\text{rate of generation}) = (\text{rate of accumulation}). \quad (1)$$

Our choice of the control volume (e.g. whole reactor, reactor section or differential element) to which Eq. (1) is applied determines the level of sophistication of our reactor model. Neglecting gradients in concentration in all spatial directions, or recognizing them only in the principal flow direction, leads to ideal reactor models of the continuous stirred tank reactor (CSTR) and plug flow reactor (PFR), respectively. Allowing for eddy transport in addition to convection leads to dispersion models, acknowledging experimentally observed time averaged flow patterns and variations around them yields phenomenological models, and finally a full description of the flow field via Navier–Stokes equations leads to fundamental models. In addition to these various levels of flow pattern description, each of which allows us to describe the input and output terms in Eq. (1) at various levels of scrutiny, we need the proper description of kinetics and microscale transport effects on it, which then enables us to properly quantify the species generation term in Eq. (1). Needless to say, in a balanced approach we should describe all terms at the same level of accuracy. It certainly does not pay to have the finest description of one term in the balance equation if the others can only be very crudely described.

For example, in combustion reactions the mechanistically based detailed description of kinetics via elementary reactions has required that plug flow and stirred tank type of flow models be abandoned in favor of computational fluid dynamics (CFD) description of the flow field [1]. An improvement in accuracy, and a more detailed description of the molecular scale events (description of the rate of generation term in Eq. (1)) has in turn forced a more detailed description of the flow field (input–output terms in Eq. (1)). In catalytic processing of multiphase systems the same trends are observed. As the level of knowledge regarding kinetics on a particular catalyst type is improved (e.g. reforming, HDS, catalytic cracking, etc.) there is a push for improved description of transport and flow in the reactors that employ such catalysts. These improvements, resulting from systematic application of CRE, are most visible in refinery operations. This is not surprising since there is a long history of research in catalysis and reactor types which are relevant to refineries. In addition, the large volumes of materials processed provide a powerful incentive for improved efficiency which is only reachable via a systematic CRE approach. In contrast, specialty chemicals and pharmaceutical processes are ''messier'' and much more poorly understood, the volume of materials is small and incentives for proper application of CRE are only starting to emerge [2].

In addition to continuing more detailed and fundamental studies of kinetics, of fluid flow and of transport processes, which are needed, new trends are evident in practice of CRE during the last few years, and it is some of these trends that I will attempt to discuss in this brief review.

2. Old and new approaches

Application of basic conservation laws (e.g. Eq. (1)) to describing catalytic reactors is certainly not a novel concept. So what is then new in catalytic reaction engineering? Basically three things: a new simultaneous approach to the problem of catalyst and reactor selection, the enhanced level of understanding used in describing the various terms of the balance equations, and consideration of novel modes of reactor operation. The old approach in catalytic reaction engineering was sequential. Usually a team of chemists would identify a catalyst suitable for the process under consideration. A team of chemical engineers then would be given a task to accommodate that catalyst form in a suitable reactor type. Proof of concept was obtained in a pilot plant, and often multiscale pilot plant experiments, if one dealt with the new process, were conducted including semiworks. Separation trains were designed to accommodate the reactor.

Now-a-days the above sequential approach is being slowly abandoned as too time consuming and too costly. A new parallel approach is used in which a multidisciplinary team consisting of chemists, chemical, environmental and mechanical engineers, and often physicists, attacks various parts of the problem simultaneously. This includes an investigation over a myriad of scales, such as molecular level description of kinetics, micro level models for transport effects on local rates, meso scale descriptions of mixing and flow and their effect on the reactor performance, macro description of the reactor and its integration with the rest of the units in the plant, and mega scale effects of the process on the environment. Most importantly, from the catalytic reaction engineering point of view, the catalyst development and reactor selection now proceed hand-in-hand. Based on this effort in parallel, attempts are often made to commercialize the process directly based on laboratory scale data. These new paradigms have become prevalent in modern chemical engineering [3,4].

Unfortunately, I am not in the position to best illustrate the transition from sequential to parallel approach in catalyst and catalytic reactor selection for several reasons. First, this is a team effort conducted in industry, and as an academician I only get exposed to it sporadically as consultant, and hence, cannot reveal the pertinent information. Second, this type of effort is still kept proprietary by companies and details will not be emerging for several years to come. Therefore, I will focus on the other two new trends in catalytic reaction engineering which regard changes in our level of description of the phenomena occurring in catalytic reactors and ways in which we choose to operate the reactors. These trends can best be illustrated via examples. I have chosen to discuss briefly three areas: flow patterns in multiphase reactors, novel modes of reactor operation, and combined reactor-separation concepts. Each of these is treated below.

3. Flow patterns and contacting in multiphase reactors

3.1. Packed beds and two-phase flow

The most frequently used reactors of this type are trickle beds, where gas and liquid reactants flow cocurrently downward through the catalyst packing. The importance of trickle beds to petroleum, petrochemical, chemical and other industries, attracted numerous research and review papers of which I will cite a few representative ones [5–10]. It has always been understood that good flow distribution and catalyst contacting is essential for good performance of trickle beds and prevention of hot spots. Recent work has shown that there are two components to this requirement: good reactor scale liquid distribution, and good local catalyst particle liquid–solid contacting [6]. Advances have been made in computing reactor scale liquid distribution via computational fluid dynamic codes [11]. However, multiphase flow codes still contain many uncertain closure schemes and descriptions of constitutive forms. Hence, research is in progress to quantify these based on first principles. Even the currently available relatively primitive forms for the phase interaction terms, like the drag, can do a good job in predicting reactor scale liquid distribution provided the catalyst bed voidage distribution is known. How to predict the distribution and configuration of the bed voidage is a still unanswered but important question. Nevertheless, CFD programs are invaluable in providing guidance for the needed number and location of quench boxes and liquid redistributors.

The particle scale incomplete wetting is now well understood, although the prediction of contacting efficiency (i.e. fraction of external catalyst area effectively wetted by liquid) still rests on an empirical correlation, based on a phenomenological model [12] rather than on a purely fluid dynamic approach. However, the validity of this correlation has been proven as well as its utility. A number of research groups [13,14] have shown that when this external wetting efficiency correlation is incorporated into reactor models, the models are capable of predicting reactor performance for both gas and liquid limited reactions [15,16]. This is not an easy task since for liquid limited reactions increased catalyst wetting improves conversion, while for the gas limiting ones exactly the converse is true [15].

Failing to identify the limiting reactant can lead to failure in scale-up. For example, equal LHSV (liquid hourly space velocity) is used as a scale-up rule for HDS and similar operations, where a dilute nonvolatile liquid reactant is processed at high hydrogen

pressure. The plant reactor, being taller than the experimental or pilot plant unit, at the same LHSV has a much larger liquid mass velocity which causes improved contacting efficiency. This improved contacting increases the catalyst effectiveness factor in the commercial unit as the supply of the liquid reactant to the catalyst is improved in the commercial reactor. This effect is properly predicted by the catalyst contacting correlation for all liquid reactant limited systems [16]. The same scale-up rule of equal LHSV was employed for aldehyde hydrogenation at modest pressures of hydrogen. The desired aldehyde conversion of 90% was readily reached in the laboratory reactor of 3.41 cm in diameter and 23.5 cm tall at LHSV of 1.3. At these conditions, the liquid superficial mass velocity in the laboratory unit was 0.06 kg/m^2 s. At the temperature and pressure conditions used in the reactor, catalyst contacting efficiency can be estimated at η_{CE}=0.6 using the correlation of [12]. The plant reactor with a diameter of 45.5 cm and 19.4 m tall was selected based on the same LHSV. The same pressure, temperature and hydrogen/aldehyde ratio were used as in the laboratory unit and, of course, the same catalyst particles were employed. The conversion was a dismal 40% instead of the design conversion of 90%. Had one recognized that in this process it was the hydrogen (gas phase reactant) that, due to the relatively low pressure employed, is the limiting reactant, this result could have been avoided. At equal LHSV, the liquid mass velocity in the plant reactor is increased to 6 kg/m^2 s causing the external contacting efficiency to rise to unity (η_{CE}=1). While this would have helped to achieve an increase in the catalyst effectiveness factor for a process where liquid reactant is rate limiting, it has exactly the opposite effect for the gas limited reaction, as the increasingly wetted external catalyst area provides an additional resistance for the gas reactant to reach the catalyst pellet. Let me illustrate this quantitatively.

If we assume a first-order gas limited reaction then, based on a plug flow model with no reactor scale maldistribution, the conversion of the liquid reactant (aldehyde) is given by

$$x_B = \frac{vA^*(1-\epsilon_B)3600k_{app}}{B_{lo}\mathrm{LHSV}}, \tag{2}$$

where x_B is the aldehyde conversion, v the stoichiometric coefficient ratio of aldehyde to hydrogen, ϵ_B the bed porosity, B_{lo} the aldehyde concentration in the liquid feed, LHSV the liquid hourly space velocity (h^{-1}) and k_{app} is the apparent first-order rate constant for a gas limited reaction (s^{-1}).

It is important to note that when identical operating conditions are used in the plant and laboratory reactors and the same LHSV is employed, then the ratio of the observed conversions equals the ratio of the observed apparent rate constants. For a gas limited reaction the ratio k_{app}/k can be shown to be approximately:

$$\frac{k_{app}}{k} = \frac{\eta_{CE}}{\Lambda_p^2/Bi_{wg} + \Lambda_p/\tanh\Lambda_p} + (1-\eta_{CE})\frac{\tanh\Lambda_p}{\Lambda_p}, \tag{3}$$

where k is the actual intrinsic rate constant, η_{CE} the catalyst external wetting efficiency, Λ_p the Thiele modulus (ratio of diffusional to kinetic resistance in a catalyst particle), and B_{iwg} is the Biot number for the transfer of gas into the particle over an externally wetted catalyst (i.e. ratio of internal gas diffusional resistance in the particle to the overall external resistance from the gas phase across the liquid layer to the pore mouths of the catalyst particle).

In the laboratory reactor at the estimated liquid mass velocity L=0.06 kg/m^2 s, the catalyst contacting efficiency [12] is approximately η_{CE}=0.6. At the plant reactor conditions at L=6 kg/m^2 s, η_{CE}=1. So we have

$$\frac{k_{app_{lab}}}{k} = \frac{0.6}{\Lambda_p^2/(Bi_{wg})_l + \Lambda_p/\tanh\Lambda_p} + 0.4\frac{\tanh\Lambda_p}{\Lambda_p},$$

$$\frac{k_{app_{plant}}}{k} = \frac{1}{\Lambda_p^2/(Bi_{wg})_p + \Lambda_p/\tanh\Lambda_p}.$$

Subscripts p and l indicate plant and lab reactor, respectively. As usual, proprietary kinetic and diffusional information needed to evaluate Λ_p or Bi_{wg} cannot be revealed. However, from the above equations it is clear that irrespective of these values we always have

$$\frac{k_{app_{plant}}}{k_{app_{tab}}} < 1$$

and that the observed conversion ratio 0.4/0.9=0.44 can readily be obtained. This is especially so since $(Bi_{wg})_p \le (Bi_{wg})_l$. For example, assume $\Lambda_p = 10$, $(Bi_{wg})_l = 10$, $(Bi_{wg})_p = 5$. Then $k_{app_{lab}}/k = 0.07$ and $k_{app_{plant}}/k = 0.333$ so that $k_{app_{plant}}/k_{app_{lab}} = 0.48$,

which is close to the observed ratio of conversions obtained in the two reactors.

It is evident that the increase in liquid holdup and the resulting increase in the liquid–solid contacting efficiency reduces k_{app} for the gas limited reaction. This means that scale-up with equal LHSV is ill advised for gas-limited reactions. If one insists on equal LHSV, then the reactor heights of the laboratory and plant reactor must also be kept the same. This leads to pancake type reactors and it is often avoided because of the potential for flow maldistribution. Clearly, for proper scale-up of gas-limited reactions a model is needed and the prediction of contacting efficiency is an important part of such a model. A methodology has also been developed, by using fines in laboratory reactors, for direct transfer of bench scale reactor data to commercial units [17].

3.2. Slurry bubble columns

These are reactors of choice for various gas conversion processes (e.g. liquid phase methanol synthesis, Fischer–Tropsch synthesis, etc.) due to their excellent heat transfer characteristics. In the past, reactor design equations rested on the assumption of ideal flow patterns (e.g. completely backmixed liquid and plug flow of gas). Currently, demands for increased selectivity and volumetric productivity require more precise reactor models, and also force reactor operation to churn turbulent flow which to a great extent is uncharted territory. While slurry bubble column performance often can be fitted with an axial dispersion model, decades of research have failed to produce a predictive equation for the axial dispersion coefficient. Recently, novel noninvasive experimental techniques have enabled us to obtain an improved understanding of the flow in these vessels, which in time will create a data base for the development of improved reactor models. For example, in our Chemical Reaction Engineering Laboratory (CREL) we have implemented Computer Automated Radioactive Particle Tracking – (CARPT) and Computed Tomography – (CT) [18–21]. CARPT allows us to map Lagrangian tracer particle trajectories throughout the column and from them extract information about instantaneous velocities, time averaged flow patterns, Reynolds stresses, kinetic energy due to fluctuating velocities, and mixing parameters such as the eddy diffusivity tensor. The combination of CARPT–CT data constitutes a basis for the verification of computational fluid dynamic (CFD) codes and for the development of appropriate phenomenologically based reactor models. Recently, utilizing CARPT data, we have succeeded in predicting the axial dispersion coefficient from the basic measured hydrodynamic quantities [22].

Our long term interest is to compile by CARPT–CT a reliable data base for liquid and slurry mixing in bubble columns and develop models for interphase exchange terms to such a point that CFD predictions for the velocity and holdup fields are in good agreement with the collected experimental observations. Since currently such CFD predictions are not possible we have addressed the following two questions. First, we wanted to know whether the collected CARPT–CT data can be utilized to predict mixing, such as quantified by an impulse tracer response in a laboratory column characterized by CARPT–CT data. Second, we wanted to know whether these findings can be extrapolated to industrial conditions.

To address the first question, CARPT data were collected in a 8 in. diameter column using air–water in churn turbulent flow. CT scans indicated an axisymmetric holdup distribution which did not change much with height for at least 3/4 length of the column (in the region about one diameter removed from the distributor and from the liquid free surface). The azimuthally averaged liquid holdup distribution is shown as a function of radius in Fig. 1(b). This holdup distribution drives a large liquid recirculation cell (Fig. 1(a)), which over most of the column's height exhibits the radial profile of the time-averaged liquid velocity shown in Fig. 1(c). The time-averaged radial liquid velocity is essentially zero in this large section of the column, where a fully developed axial velocity profile of Fig. 1(b) is present. The axial and radial eddy diffusivities, averaged azimuthally and over column height, are shown in Fig. 1(d) also [23].

All the information is now available for solving the ensemble averaged tracer continuity equation in the bubble column reactor which for a nonvolatile tracer takes the form below.

$$\frac{\partial(\varepsilon C)}{\partial t} + \frac{\partial}{\partial z}(u_z \epsilon C) = \frac{1}{r}\frac{\partial}{\partial r}\left(r\epsilon D_{rr}\frac{\partial C}{\partial r}\right) + \frac{\partial}{\partial z}\left(\epsilon D_{zz}\frac{\partial C}{\partial z}\right) \quad (4)$$

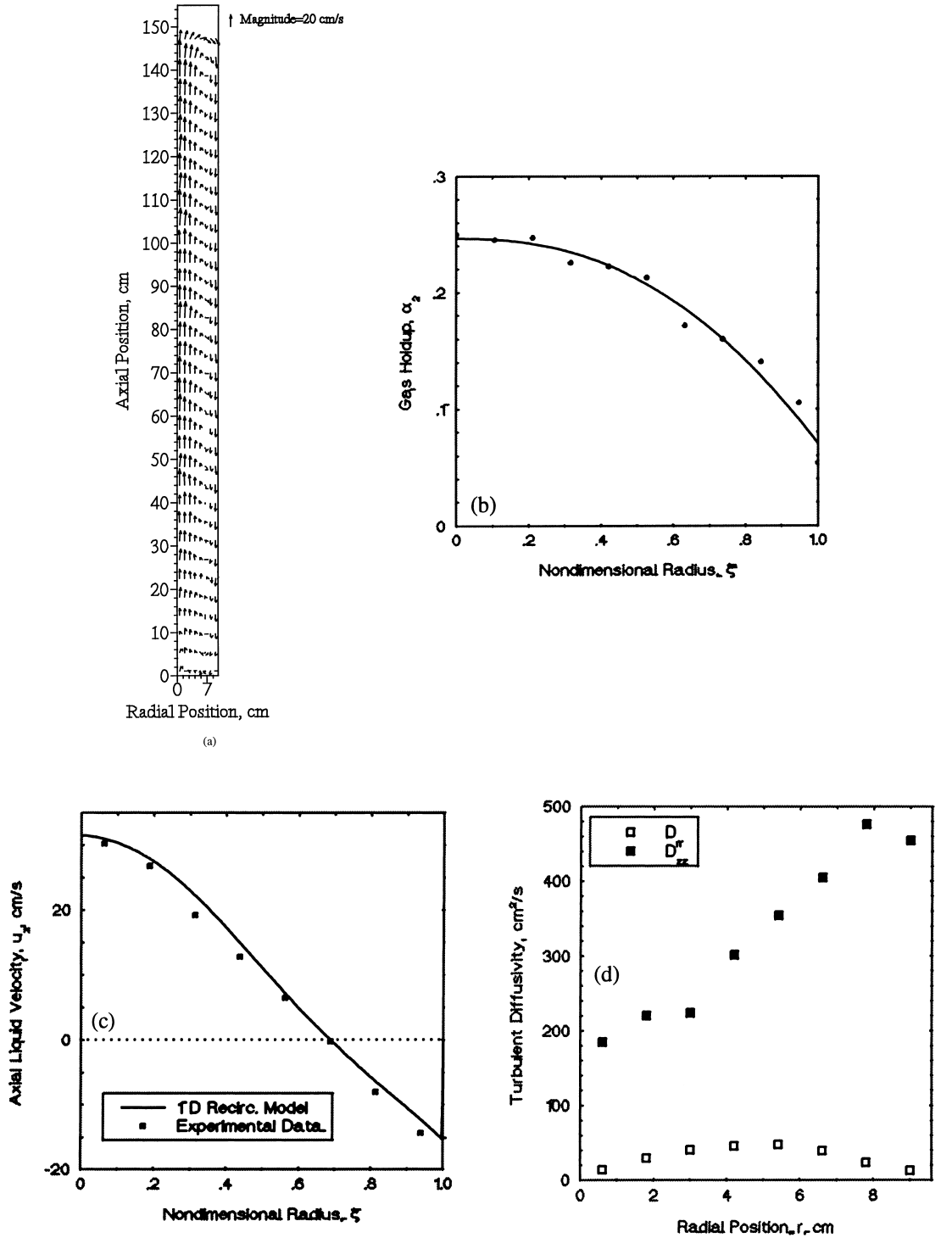

Fig. 1. Fluid dynamic parameters from CARPT-CT for 8 in. diameter column, Ug=10 cm/s, Ul=1 cm/s: (a) velocity vector plot; (b) gas holdup profile; (c) axial liquid velocity profile; (d) axial and radial turbulent eddy diffusivities.

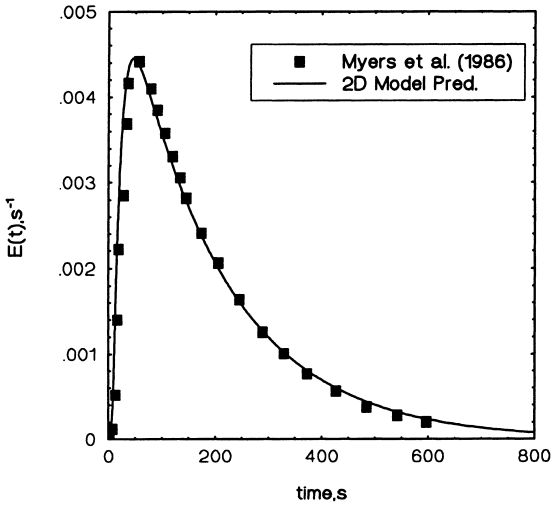

Fig. 2. Comparison of model predicted and measured liquid tracer exit age density function.

In arriving at Eq. (4) we have utilized the Bousinesq approximation and approximated the cross-correlation between fluctuating velocity components and tracer concentration with the products of the corresponding eddy diffusivity and the mass concentration gradient. Moreover, we assume that eddy diffusivities in the axial and radial direction are those measured by CARPT. Then we can solve the continuity equation for the distribution of concentration C, since the time averaged liquid holdup, ϵ, time averaged liquid velocity, u_z, axial eddy diffusivity, D_{zz}, and radial eddy diffusivity, D_{rr}, are all known. The mixing cup tracer concentration at the top of the column can then be calculated and properly normalized to provide the exit age density function for the liquid tracer. Comparison of model prediction (with no adjustable parameters) with independently taken tracer data is shown in Fig. 2. The agreement is excellent.

This illustrates that a 2D representation of an essentially distinctly 3D flow field is sufficient to predict the overall tracer residence time distribution RTD. The successful extension of this procedure in the interpretation of industrial reactor tracer data has been recently demonstrated by Degaleesan et al. [22,23]. This procedure can be extended to account for reaction in the slurry phase by adding reaction terms to Eq. (2).

4. Novel modes of operation

4.1. Reverse flow

Process industry is a conservative one but increased competitiveness and globalization has created an impetus for change. For example, catalytic fixed-bed tubular reactors have been traditionally operated at steady state. Over a decade ago Boreskov and co-workers [24,40], at the Institute of Catalysis at Novosibirsk, Russia, documented the advantages of reverse flow periodic operation. Such an operation creates a favorable temperature profile for exothermic reactions, allowing higher conversions. It also allows temperatures in the middle of the reactor to reach many multiples of the adiabatic temperature rise. Hence, reverse flow operation makes it possible catalytically to combust very lean fuel mixtures. Both phenomena have been taken advantage in commercial operation, such as in a reverse flow sulfuric acid plants and in reverse flow catalytic VOC abatement process. Recently, in CREL the concept of an asymmetric periodic reverse flow reactor was developed [25]. This concept combines an exothermic reaction, which heats the bed during each odd semicycle, and an endothermic reaction, which cools the bed during each even semicycle. Theoretical regions of operability have been identified and potential for methane reforming was investigated [25–27]. High thermal efficiency and stable operation are possible based on modeling studies. It is interesting to note that while the theoretical concept of ''asymmetric'' periodical flow reversal that couples exothermic and endothermic reactions was thoroughly explored in CREL, it has already been implemented in commercial practice. ABB Lummus apparently applied this concept to catalytic dehydrogenation and regeneration of the catalyst [28,29].

4.2. Recirculating fluidized bed

Partial oxidation processes traditionally were conducted in packed-bed wall cooled tubular reactors. The new process for butane oxidation to maleic anhydride employs a riser reactor for the reaction part and fluidized beds for the catalyst regeneration. The catalyst instead of being exposed to a steady state gas concentration and temperature profile is now being cycled between a reaction and regeneration zone not

unlike catalytic cracking in petroleum refining. Both, reliable models and data for catalyst–gas contacting and for the extent of catalyst backmixing in the riser and regenerator are needed, coupled with catalytic reaction mechanism and kinetics, to assess the performance of such recirculating loops. This is especially important since a number of processes may utilize this technology in the future.

4.3. Countercurrent flow and induced pulsing flow

Traditionally trickle beds operate with cocurrent downflow of gas and liquid at steady state. However when high conversions are required and the gaseous byproduct of reaction is known to inhibit the rate, such as in hydrodesulfurization, countercurrent flow is to be preferred. The effect of such an operation on volumetric productivity, selectivity and operability is currently under investigation by a number of companies. Moreover, to improve liquid–solid contacting at low liquid mass velocities in the cocurrent downflow mode, a concept of induced pulsing, triggered by periodic switching of the liquid flow between high and low, has been proposed and investigated [30,31]. The timing of transferring these ideas to commercial practice is a well-guarded proprietary information. Nevertheless, these studies provide an impetus for renewed characterization of different catalyst particle shapes on pressure drop and liquid distribution in beds with either countercurrent flow or induced pulsing flow.

4.4. Combining reaction and separation in the same vessel

The traditional approach in chemical processing has been to do one operation at the time, e.g. prepare the feed for the reactor, conduct the reaction, separate components from reactor outflow, etc. All of these operations are typically conducted in separate vessels. The new trend is in combining some of them in a single vessel, especially separations and reactions. A good review of such multifunctional reactors was provided by Westerterp [32]. To accomplish reaction and separation in a single vessel three main ideas have been explored. They are: reactive or catalytic distillation, membrane reactors, and trickling solids adsorbents in packed beds. Let us briefly consider each of them.

4.5. Reactive and catalytic distillation

The main idea here is to develop a catalyst that is active in the temperature range of boiling points of reactants and products. Such a catalyst can then be used in a packed-bed catalytic distillation column where products can be removed in situ. This allows high conversion of reactants per pass since locally the equilibrium limitation of the product is overcome by product removal. The concept has been successfully commercialized, both in petroleum processing, where packed-bed catalytic distillation columns are used, and in manufacture of chemicals where reactive distillation is often employed [33–35]. Eastman Company pioneered reactive distillation in commercial practice while ABB Lummus offers catalytic distillation packages for refiners. The next generation of commercial processes utilizing catalytic distillation technology will be in the area of MTBE production and in the manufacture of other oxygenates and fuel additives.

4.6. Membrane reactors

Many books and innumerable papers have been written on membrane reactors [36,37]. The paper by Hsieh [38] documents the state of the art well. The impetus for using membrane reactors is rather diverse. Some simply attempt to use membranes for a distributed feed of one of the reactants to a packed-bed of catalyst, such as in partial oxidation reactions in order to improve selectivity. Others have attempted selective product removal to remove equilibrium limitations. Hence, results have been reported in the literature on catalytic permselective membrane reactors (CMR), catalytic nonpermselective membrane reactors (CNMR), packed-bed permselective membrane reactors (PBRM), packed-bed catalytic permselective membrane reactors (PBCMR), fluidized bed permselective membrane reactors (FBMR) and fluidized bed catalytic permselective membrane reactors (FBCMR).

It is a fair question to ask whether this intensive research effort on membrane reactors has resulted in commercialization of the concept? As far as the open literature is concerned the answer is negative. We are all aware of the tremendous positive impact that membrane separations have already had on chemical, petroleum and pharmaceutical processing, and that

membranes have an additional enormous potential in separations. However, in reactor applications the future is less certain, and applications await the solution of two basic problems. First, material scientists must solve the problem of providing inorganic membranes of perfect integrity and, yet, which will allow large fluxes of the desired species. Current fluxes are simply by order of magnitude inadequate for current reactor demands on reactor volumetric productivity. Second, chemical engineers must figure out the heat transfer problem which now threatens successful scale-up. Only when these two problems are solved will catalytic membrane reactors be commercialized. While I do not have a crystal ball as to in which reaction system, if any, catalytic membranes will find their first commercial application, due to great successes in air-separation it would seem reasonable to expect membrane reactors that combine oxygen transfer membranes with selective catalytic layers for partial oxidation of hydrocarbons.

4.7. Trickling solids adsorbents

In this novel reactor fine particles of solid adsorbent trickle through a packed-bed of catalyst counter currently to the gas stream of reactants and products. This allows in situ product removal and overcomes equilibrium limitations. The success of this concept was best illustrated by Kuczinski et al. [39] who managed in a pilot plant facility to achieve 100% conversion of synthesis gas to methanol in a vapor phase reactor. Unfortunately, the adsorbent used could not withstand the number of cycles needed for economic commercial application of the concept due to attrition problems. While research on better understanding of the fluid dynamics of the trickling solids reactor is needed for successful scale-up, and is in progress, the ultimate commercialization of the concept awaits breakthroughs in material science that will produce an attrition resistant adsorbent with high adsorption capacity. This of course is a nontrivial problem.

5. Concluding remarks

This was not meant to be a comprehensive review of all new trends in catalytic reaction engineering. The objective simply was to provide a flavor of the differences between the old approach and the new trends. The old approach rests on sequential catalyst and reactor selection, involving the use of conventional reactors and modes of operation, while the new parallel approach to catalyst and reactor selection rests on improved molecular level understanding of the catalyst as well as on better understanding of fluid dynamics and transport and explores innovative modes of operation. An example of the new approach is the plant that DuPont built in Spain for maleic anhydride production in a fast recirculating fluidized bed reactor. An attrition resistant catalyst (this indicates hope for trickling adsorbents) was developed simultaneously with the reactor concept to replace the classical packed-bed process. Successful commercialization required not only a good understanding of catalysis, but also of material science (in order to make the catalyst attrition resistant) and of reactor fluid mechanics. Process development clearly has become an interdisciplinary effort.

The examples cited in this brief review confirm the following new paradigms and trends in catalytic reaction engineering.

1. Improved understanding and quantification of transport-kinetic interactions on single catalyst particle scale and reactor scale is necessary for establishing fundamentally based models for catalytic reactors. Such models have predictive ability for scale-up and scale-down. Successful implementation was demonstrated for trickle beds and slurry bubble columns.
2. Computational power and advances in instrumentation allow us to elevate catalytic reactor modeling in catalytic reaction engineering to the level of science and scrutiny utilized in catalytic research. The two must go hand in hand for successful innovation on the process level and for economically optimal commercialization.
3. Our improved understanding of the transport-kinetic interactions in various reactor types allows us to search for novel operational strategies and combination of reactions and separations in the same vessel.

Some attractive options for improved catalytic reactor performance via novel modes of operation are:

1. Periodic (symmetric) operation of packed beds with exothermic reaction.

2. Coupling of an exothermic and endothermic reaction in a periodically operated (asymmetric) packed-bed.
3. Induced pulsing in trickle beds.
4. Counter-current flow in gas–liquid–solid catalyzed beds.
5. Recirculating loop reactors with catalyst regeneration.

In situ reactor separations are also attractive and can be achieved via:

1. Catalytic distillation.
2. Membrane reactors.
3. Trickling solids adsorbent.

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