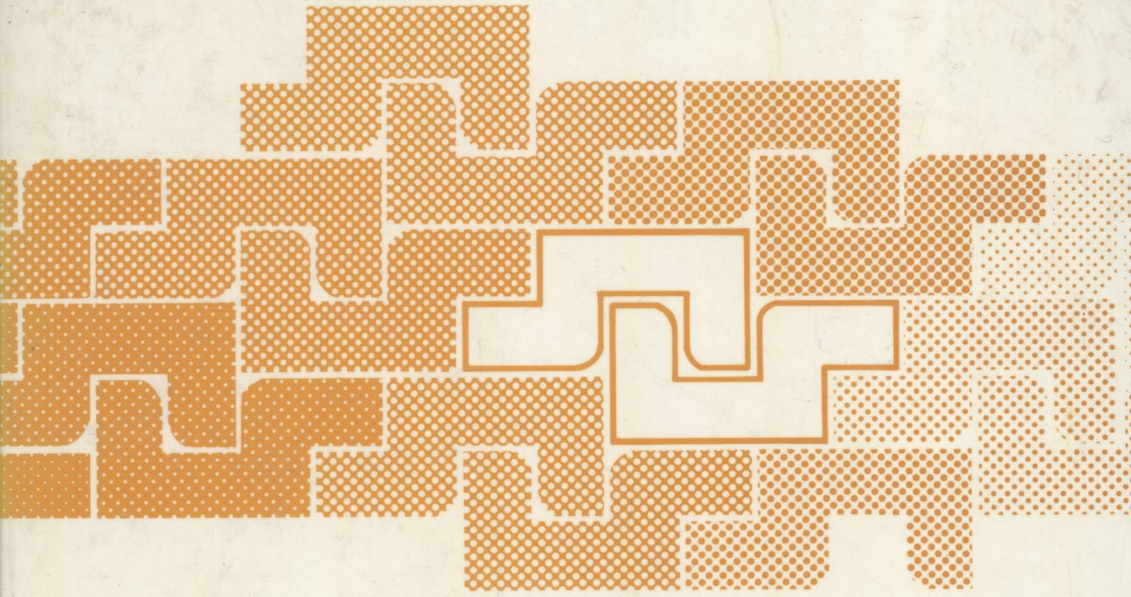

Chemical Reactor Design and Technology

Edited by

Hugo I. de Lasa

NATO ASI Series

Chemical Reactor Design and Technology

Overview of the New Developments of Energy and Petrochemical Reactor Technologies. Projections for the 90's

edited by

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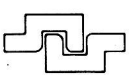

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NATO ADVANCED STUDY INSTITUTE

ON

CHEMICAL REACTOR DESIGN AND TECHNOLOGY

Overview of the New Developments of Energy and Petrochemical Reactor Technologies. Projections for the 90's

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PREFACE

Today's frustrations and anxieties resulting from two energy crises in only one decade, show us the problems and fragility of a world built on high energy consumption, accustomed to the use of cheap non-renewable energy and to the acceptance of existing imbalances between the resources and demands of countries. Despite all these stressing factors, our world is still hesitating about the urgency of undertaking new and decisive research that could stabilize our future. Could this trend change in the near future? In our view, two different scenarios are possible. A renewed energy tension could take place with an unpredictable timing mostly related to political and economic factors. This could bring again scientists and technologists to a new state of shock and awaken our talents. A second interesting and beneficial scenario could result from the positive influence of a new generation of researchers that with or without immediate crisis, acting both in industry and academia, will face the challenge of developing technologies and processes to pave the way to a less vulnerable society.

Because Chemical Reactor Design and Technology activities are at the heart of these required new technologies the timeliness of the NATO-Advanced Study Institute at the University of Western Ontario, London, was very appropriate. For instance, processes such as the transformation of renewable resources (wood and biomass), the conversion of less critical ones (coal, natural gas, heavy crudes) and the chemical changes following these transformations (synthesis and conversion of methanol, synthesis of hydrocarbons, synthesis of ammonia) could be objectives for new chemical reactors. We perceive this hour as a time of action for a generation of researchers who could innovate in Chemical Reactor Engineering. We believe as well that these novel approaches will result in a more effective interaction and communication between industry and academia, between various countries and between researchers in organizations. It will possibly be necessary in the future to reformulate the research action placing more emphasis upon an interdisciplinary approach. With these goals in mind we planned the NATO Advanced Study Institute meetings involving lecturers and participants from several countries, from both university and industry, and from various organizations.

It should be stressed that Chemical Reactor Technology for processes involving catalytic and non-catalytic reactions evolved in recent years in numerous directions and options. Because of the diversity of topics, the selection of subjects and lecturers proved to be a challenging and complex task. We decided to settle on a compromise, focusing the scope of the ASI on the more representative types of reactors and the more significant associated technological problems. The main areas of concentration for the ASI were then: fixed bed reactors, fluidized beds (two and

three phase), - slurry reactors, - trickle beds, - transport in catalysts, - kinetic data analysis, - mixing and tracer techniques, - bubble column reactors, - specific applications (hydrocracking of petroleum residua, ammonia and methanol synthesis reactors).

The final program for the NATO-ASI covered in summary the present status of Chemical Reactor Design and Technology, novel ideas, new strategies and their projections for the coming decade. These matters were considered through an intense program of activities which included 15 formal lectures, two poster sessions with 23 presentations, 3 laboratory demonstrations with 6 experiments, 3 special panel discussions and 2 talks delivered by special invited speakers.

The participants had the opportunity to contribute to the NATO-ASI during the Poster Session. Posters covering a wide range of subjects were presented: non-isothermal trickle beds, catalyst deactivation, mixing in fluidized beds, control of chemical reactors, maldistribution in chemical reactors, cyclic operation in trickle beds, polymerization reactors, etc. The most relevant contributions of the Poster Session were selected to be included in this NATO-ASI Proceedings.

Another important activity of the NATO-ASI was the Panel Discussion. Three panels were organized on tracer techniques, trickle beds and slurry reactors and fluidized bed reactors. Each panelist delivered a short presentation indicating points to be clarified, crucial issues, novel ideas. The short talks were followed by discussion periods with active participation of the audience and panelists. Six laboratory demonstrations were also presented at the University of Western Ontario on the following subjects: - entrainment and grid leakage in fluidized beds, - ultrapyrolysis process for the conversion of biomass, - fast catalytic cracking and regeneration using the pulse technique, - mass transfer and bubble phenomena in three-phase fluidized beds, - novel configuration for fixed bed reactors. It was possible to show with these laboratory demonstrations basic principles, advanced instrumentation, novel reactors, applications, strategies for scaling-up.

The dinners of the NATO-ASI Conference provided a forum for the review of future trends and strategies. Two Special Invited Speakers, Dr. J. Grace and Dr. J. Wright, delivered talks about Research Needs in Chemical Reactor Engineering and Role of Universities and Research in High Technology Development in Canada.

In summary, the NATO-ASI held at Spencer Hall, London, Ontario was a massive learning experience where both participants and lecturers found the appropriate atmosphere for fruitful technical exchanges and for visualizing the technological changes in Reactor Engineering for the 90's.

Here I would like to express my gratitude to the members of the Advisory Committee, Prof. A. Rodrigues, Prof. J.R. Grace, Prof. M.A. Bergougnou, Dr. R. Koros and Dr. M.A. Ternan who co-operated in many ways in the difficult task of selecting the lecturers and organizing the NATO-ASI meeting.

My special thanks should be addressed to the Local Organizing Committee, graduate students of the University of Western Ontario who helped so effectively with the numerous organizational tasks of the NATO-ASI Conference.

A special acknowledgement to the participants from industry and academia who contributed with remarkable enthusiasm and interest to make our meeting a successful forum for the exchange of technical views in Chemical Reactor Engineering.

I would like to express my sincere thanks to the NATO Scientific Affairs Division who supported financially the NATO-ASI Conference. I would like to gratefully acknowledge as well the financial contribution of the Natural Sciences and Engineering Research Council of Canada.

My appreciation to Prof. K. Shelstad, Faculty of Engineering Science, The University of Western Ontario, for his most valuable contribution in the process of reviewing the papers included in this book.

Finally my deepest gratitude to my wife, Graciela, who provided all the cooperation and inspiration needed for the success of this event.

London, Ontario, Canada Hugo de Lasa

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TRANSPORT PROCESSES IN CATALYST PELLETS

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INTRODUCTION

The subject of reaction and diffusion in porous catalysts is now a well established branch of knowledge discussed in several books such as by Aris [1] and Jackson [2]. Its practical importance has long been recognized since the pioneer work by Thiele [3].

In this paper we will first review some basic concepts and apply them to the design of isothermal reactors working in the diffusional regime. Then we will concentrate our attention on the problem of intraparticle convection in large pore catalysts. Several aspects of this question will be dealt with - effectiveness factors for iso - thermal and nonisothermal catalysts, measurement of effective diffusivities and the implication of intraparticle convection effects on the design and operation of fixed bed catalytic reactors.

From a qualitative analysis of the competition between reaction and diffusion in an isothermal pellet one easily recognizes that the parameter governing the steady state behavior of the pellet is the ratio between time constants for diffusion and reaction, i.e., τ_d/τ_r. If $\tau_d \ll \tau_r$ the reaction rate is much slower than the diffusion rate; the concentration profile inside the pellet is then almost flat and equal to the external surface concentration. The effectiveness factor is around unity. However, when $\tau_d \gg \tau_r$ the concentration inside the pellet will be lower than the external surface concentration and the effectiveness factor will be lower than one provided the reaction order is $n > 0$. In the first situation the catalyst is working in the kinetic controlled regime; in the second case the catalyst is operating in the diffusion controlled regime. We can easily recognize that the Thiele modulus ϕ is such that $\phi^2 = \tau_d/\tau_r$ with $\phi = \ell(kc_s^{n-1}/D_e)^{1/2}$ for irreversible n^{th} order reactions.

The mathematical model for diffusion and reaction in a homoge - neous isothermal catalyst where a first order,irreversible reaction occurs is:

$$\frac{d^2f}{dx^2} + \frac{s-1}{x}\frac{df}{dx} + \phi^2 f = 0 \qquad (1a)$$

$$x=1 \quad , \quad f=1 \qquad (1b)$$

$$x=0 \quad , \quad df/dx=0 \qquad (1c)$$

where $f=c/c_s$ is the reduced concentration inside the pellet, $x=z/\ell$ is the reduced position in the pellet (ℓ is the half thickness of a slab or the radius of a sphere) and s is a shape factor (s=1,2 and 3 for slab,infinite cylinder and sphere,respectively).

For a slab catalyst the concentration profile inside the pellet is:

$$f= \cosh(\phi x) \; / \; \cosh \phi \qquad (2)$$

and the effectiveness factor is:

$$\eta= r_{obs}/r_s(c_s)=th\phi/\phi \qquad (3)$$

For strong diffusional regime $\eta \simeq 1/\phi$.Whatever the shape is we get:

$$\eta \simeq s/\phi \qquad (4)$$

For zero order reactions one should take into account that r=k only if c> 0;otherwise r=0. In a situation where the concentration reaches a zero value inside the particle at a point x=x* we should replace the boundary condition (1c) by f=0 and df/dx=0 at x=x*.The effectiveness factor is now simply the ratio of the "utilized" particle volume and the total particle volume,i.e.,$\eta=1-x^*$. In the kinetic controlled regime $\eta \simeq 1$ and in the pure diffusional regime $\eta \simeq \sqrt{2}/\phi$. Again for any shape we get:

$$\eta \simeq s\sqrt{2}/\phi \qquad (5)$$

In general for irreversible nth order reactions the catalyst effectiveness factor in the diffusional regime is:

$$\eta \simeq s\sqrt{2/(n+1)}\;/\phi \qquad (5a)$$

Before going on to discuss the importance of the effectiveness factor for reactor design let us briefly emphasize the point that we need in the previous treatment to know the Thiele modulus (and hence the kinetic constant k) in order to calculate η. In practice

the true kinetic constant can be obtained from various experiments carried out with different particle sizes.However this is a time consuming procedure.What we need is a method to calculate the effectiveness factor by doing just one kinetic experiment with a real catalyst and thus measuring r_{obs}.This can be done because as pointed out by Weisz [4] $\eta\phi^2=\ell^2 r_{obs}/D_e c_s$ involves only measurable quantities and the function $\eta=f(\eta\phi^2)$ is known.

Let us discuss now the implication of the catalyst effectiveness factor on reactor design.The simplest situation is obviously that in which there are no diffusional limitations.Then the amount of catalyst needed to get a given conversion is:

- for a CSTR

$$W_A = F_{Ao} X_e / r'(X_e) \tag{6a}$$

- for a plug flow reactor

$$W_P = F_{Ao}\int_0^{X_e} \frac{dX}{r'(X)} \tag{6b}$$

with the reaction rate r' is expressed in mole/gcat.s .

If mass transfer resistances are important then the actual mass of catalyst needed to get the same conversion is $W'=W/\eta$.In summary, with a given amount of catalyst the conversion at the outlet can be calculated through the so-called "design equations" extended below to the case where we have strong diffusion effects:

o Zero order reaction r'=k;slab catalyst (Rodrigues et al.[5])

Perfectly mixed reactor or CSTR

- kinetic controlled regime $X_{Ak}=N_r$ (7a)
- diffusion controlled regime $X_{Ad}=\sqrt{\alpha^2+2\alpha}-\alpha$ (7b)

In these formulae $N_r=Da_I=\tau/\tau_r=k\rho_b\tau/c_{in}$ (number of reaction units or Damkholer number), $\alpha=N_r N_d=(Da_I/\phi)^2$, $N_d=\tau/\tau_d=D_e\tau/\ell^2$ (number of diffusional mass transfer units). Equation (7b) is only valid for $N_r \geq 2N_d/(1+2N_d)$.

Plug flow reactor

- kinetic controlled regime $X_{Pk}=N_r$ (8a)
- diffusion controlled regime $X_{Pd}=\sqrt{2\alpha}-\alpha/2$ (8b)

Equation (8b) is valid for situations in which $N_r \geq 2N_d/(1+ N_d/2)^2$. Figure 1 shows the conversion obtained in a CSTR and a plug flow reactor when the catalyst is working in the pure diffusional regime.

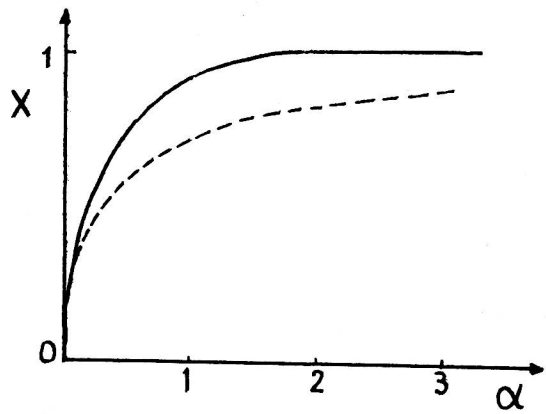

Figure 1 - Conversion X as a function of α (catalyst working in the diffusional regime) [5]

____ plug flow reactor

---- CSTR

We observe that only one parameter α governs the steady state behavior of ideal reactors provided the catalyst is working in pure diffusion regime. Moreover, in a plug flow reactor, there is a critical value for α (or in practical terms a critical height for the reactor) at which complete conversion is obtained, i.e., $\alpha=2$. This is because for the diffusional regime a zero order reaction is equivalent to a 1/2 order reaction in the kinetic regime.

o First order reaction r'=kc;slab catalyst

CSTR

The conversion is now $X_A = \eta\, Da_I/(1+ \eta\, Da_I)$ where $Da_I = N_r = k\rho_b \tau$ and $\eta = th(\phi)/\phi$. The limiting cases are:

-kinetic controlled regime $X_{Ak} = \dfrac{Da_I}{1+ Da_I}$ (9a)

- diffusion controlled regime $X_{Ad} = Da_I/(\phi+Da_I) = \sqrt{\alpha}/(1+\sqrt{\alpha})$ (9b)

Plug flow reactor

The conversion is now $X_P = 1- \exp(-\eta\ Da_I)$ .The limiting situations are:

- kinetic controlled regime $X_{Pk} = 1- \exp(-Da_I)$ (10a)

- diffusion controlled regime $X_{Pd} = 1-\exp(-Da_I/\phi) = 1-\exp(-\sqrt{\alpha})$ (10b)

If we know the conversion for an ideal plug flow reactor without diffusion limitations X_{Pk} and the actual Thiele modulus ϕ we can easily calculate X_{Pd} by taking into account that $1-X_{Pd} = (1-X_{Pk})^{1/\phi}$.

In summary:the steady state behavior of these reactors is then governed by three time constants:

τ - space time or time constant for the reactor

τ_r - time constant for the reaction

τ_d - time constant for diffusion

INTRAPARTICLE AND EXTERNAL CONCENTRATION AND TEMPERATURE GRADIENTS

At a point in the reactor one should consider the competition between reaction,mass and heat transfer inside the catalyst and also in the film around the catalyst particles.An important step in reactor design is the a priori estimate of external and intraparticle gradients of concentration and temperature.These values can be a guide for the choice of a reactor model.

Let us recall how to calculate such gradients:

Concentration gradients

o Intraparticle

$$\frac{c_{Ab} - c_{As}}{c_{Ab}} = \frac{r_{obs}\ \ell}{k_f\ c_{Ab}} = \bar{\eta}\ \overline{Da}_{II} \qquad (11a)$$

o External (film)

$$\frac{c_{As}}{c_{Ab}} = 1- \bar{\eta}\ \overline{Da}_{II} \qquad (11b)$$

where $\bar{\eta} = r_{obs}/r_b(c_{Ab},T_b)$ and $\overline{Da}_{II} = k(T_b)\ell/k_f$.

Temperature gradients

o Intraparticle

$$\frac{T_{max}-T_s}{T_s} = \beta \quad \text{or} \quad \frac{T_{max}-T_s}{T_b} = \bar{\beta}(1-\bar{\eta}\,\overline{Da}_{II}) \tag{11c}$$

o External(film)

$$\frac{c_{As}}{c_{Ab}} = \bar{\beta}\, b \tag{11d}$$

where $\beta=(-\Delta H)D_e c_{As}/\lambda_e T_s$ (Prater thermicity factor), $\bar{\beta}$ is referred to bulk conditions and $b=Bi_m/Bi_h=(k_f \ell/D_e)/(h\ell/\lambda_e)$.

The formulae presented above are based on ideas put forward by Damkholer. From analysis of the competition between reaction, heat and mass transfer (diffusion) inside catalysts he obtained an equation which relates temperature and concentration at a point within the pellet, i.e.,

$$T-T_s = \frac{(-\Delta H)D_e}{\lambda_e}(c_{As}-c) \tag{12}$$

Obviously the maximum temperature inside the pellet occurs at c=0.

Similarly, the temperature difference in the film is related to the concentration difference by:

$$T_s-T_b = \frac{(-\Delta H)\,k_f}{h}\,(c_{Ab}-c_{As}) \tag{13}$$

where k_f is the film mass transfer coefficient and h is the film heat transfer coefficient.

Practical values of the parameters governing the behavior of a catalyst pellet are:

Prater thermicity factor ($\bar{\beta}$)	$-1 < \bar{\beta} < 1$
Arrhenius number ($\bar{\gamma}$)	$5 < \bar{\gamma} < 40$
Thiele modulus (ϕ)	$10^{-2} < \phi < 30$
Lewis number for the catalyst, $Le_c=(\lambda_e/\rho_c c_{pc})/D_e$	$10 < Le_c < 10^4$
Adiabatic temperature rise (dimensionless) $B=(-\Delta H)c_o/\rho_f c_{pf} T_o$	$10^{-2} < B < 10$
$b=Bi_m/Bi_h$	$10 < b < 10^4$ gas/solid $10^{-4} < b < 10^{-1}$ liquid/solid