

# **Distribution of functionalities at different scales within a multifunctional reactor**

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*Dedicated to my beloved family & friends*

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# Abstract

The performance of heterogeneous catalyst systems are influenced by mass and heat transport phenomena occurring in the catalyst pellet. Although, in general, transport resistances may be viewed as detrimental to the performance of catalysts, it has been demonstrated that a prudent structuring of catalyst activity within the pellet can actually exploit the transport limitations to enhance process performance (Morbidelli, et al., 1982). Analogous spatial structuring studies have also been carried out at a reactor level.

This work highlights the potential benefits of a structured distribution of functionalities in multifunctional reactor systems at both the pellet and reactor levels. The concept of spatial structuring in multifunctional reactors is illustrated using two case studies – adsorptive reactors for the Claus process and bifunctional catalysts for styrene synthesis using oxidative reheat technology. The “approach to equilibrium” is a useful parameter to analyse how structuring can be carried out expediently within a reactor. The following key conclusions can be drawn from the work done:

- structuring is crucial decision variable for any multifunctional reactor
- optimal distribution of functionalities at a reactor level (macrostructuring) improves the reactor performance and sometimes, the optimal macrostructure may be simply a uniform distribution of functionalities along the reactor length
- integration of functionalities at the pellet level circumvents transport limitations and improves the overall reactor performance
- microstructuring can improve the performance of a process, though often the micro-integration of functionalities is sufficient

# Kurzreferat

Die Leistung heterogener Katalysatorsysteme unterliegt dem Einfluß von Massen- und Wärmetransportphänomenen innerhalb des Katalysator-korns. Obwohl allgemein Transportwiderstände als leistungsmindernd angesehen werden, konnte nachgewiesen werden, dass eine durchdachte Verteilung der Aktivitäten innerhalb des Katalysatorkorns die Transportlimitierung ausnutzen kann, um die Prozesseffizienz zu steigern (Morbidelli, et al., 1982). Analog wurden räumlich strukturierende Studien auf Reaktorniveau durchgeführt.

Diese Arbeit beleuchtet den potentiellen Nutzen der Strukturierung von Funktionalitäten in multifunktionalen Katalysatorsystemen, sowohl innerhalb des Katalysatorkorns, als auch des Reaktors. Das Konzept der räumlichen Strukturierung in multifunktionalen Reaktoren wird anhand zweier Beispiele illustriert: adsorptive Reaktoren für den Clausprozeß und die bifunktional katalysierte Styrolsynthese unter Einsatz oxidativer Wärmespeicher-Technologie.

Die Annäherung an den Gleichgewichtszustand ist eine hilfreiche Größe, um zu bestimmen, wie eine zweckmäßige Strukturierung im Reaktor stattfinden kann. Im Wesentlichen können die folgenden Schlüsse aus dieser Arbeit gezogen werden:

- Strukturierung ist ein ausschlaggebender Entscheidungsparameter in jedem multifunktionalen Reaktor.
- Eine optimale Verteilung von Funktionalitäten auf Reaktorebene (Makrostrukturierung) verbessert die Leistung des Reaktors und die optimale Makrostruktur kann auch einfach eine gleichmäßige Verteilung der Funktionalitäten über die Reaktorlänge sein.
- Integration der Funktionalitäten auf Katalysatorkornebene umgeht Transportlimitierungen und verbessert die Reaktorgesamtleistung.
- Mikrostrukturierung kann die Leistung des Prozesses verbessern, obwohl meist die Mikrointegration der Funktionalitäten ausreicht.

# **Chapter 1: Introduction to structuring of catalytic chemical reactors**

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## 1.1. Introduction

Being the heart of a chemical process, reactors exert a major influence on the extent of upstream and downstream processing in a chemical process. Various strategies have been developed to manipulate process variables, such as temperature, pressure, residence time and the mode of contacting, within the space and time coordinates of the chemical reactor in order to improve overall process performance. The recent advent of multifunctional reactors has opened further opportunities for enhancing reactor performance and has redefined the role of reactors in chemical processes.

Following the introduction of the multifunctional reactor concept in the late 1980s (Agar & Ruppel, 1988) and the commercial success of methyl-tertiary butyl ether (MTBE) synthesis using reactive distillation columns, there has been an exponential increase in work in the field of multifunctional reactors and a plethora of multifunctional reactor concepts has been studied. Adsorptive reactors, reactive distillation, membrane reactors, reactive chromatography, reactive filtration, reactive precipitation, reactive extraction are some of the well-known examples of multifunctional reactors which have been the subject of considerable research.

Often significant effort is expended in developing novel multifunctional reactors for a specific reaction scheme, whilst no guidelines to identify new applications for the new concept are available. In the absence of such guidelines, design engineers tend to sideline new multifunctional concepts and opt for traditional design choices, for which proven design procedures are available. Appreciating the situation, a conglomerate of research groups from the University of Dortmund undertook extensive research work to establish a methodical approach for analysing different multifunctional reactor concepts and identifying the most appropriate process designs for a given reaction system. This project, "Integrierte Reaktions- und Trennoperationen" (IRT) was funded by the German Research Council (DFG) and started in the year 1999 continuing for 6 years and concluding with the publication of its findings in a book. Reactive adsorption, reactive chromatography, reactive extraction and reactive distillation were the reactive separation processes studied in this project and this thesis was initiated within the framework of this

project and aimed to generate guidelines for integrating and structuring multiple functionalities within a pellet.

Of the multifunctional reactor concepts mentioned above, reactive adsorption provides an example in which multiple functionalities can be distributed at a pellet level and hence this work initially focussed on understanding the distribution of functionalities in an adsorptive reactor at both the pellet and reactor level. In the absence of guidelines for the distribution of multiple functionalities within a pellet, mathematical models of adsorptive catalyst pellets were developed and numerous simulation runs had to be carried out individually for a given distribution within the pellet to check whether the distribution proposed was optimal for the given reaction system. Though this approach was tedious, it brought forth very limited additional insights into the underlying problem. To acquire greater insights and speed up the process, numerical optimisation techniques were adopted to establish the best distribution of functionalities within a pellet. In simple terms, optimisation is a tool that carries out numerous simulation runs with the optimiser varying the control variables – in this case the distribution within the pellet in each iteration until the process objectives are fulfilled without violation of any process constraints. All these runs are carried out automatically without manual intervention.

This tool immensely reduced the time spent on simulation runs and assisted in arriving at the distribution guidelines for the various reaction schemes considered. The results of the work on distribution of functionalities within a pellet are summarised in Chapter 3.

The approach to equilibrium is a fundamental reaction engineering concept that provides a measure of the driving force available for a reversible reaction to occur. In an adsorptive reactor, the approach to equilibrium varies as a function of space and time, indicating that the optimal distribution within a reactor will also vary along its length. Hence the optimisation space of an adsorptive reactor is not limited to the pellet dimension alone, but it is also a function of pellet's location within the reactor. Studies have been conducted to understand the importance of the distribution of catalyst and adsorbent functionalities at the reactor level and these aspects are discussed in Chapter 2.

Moving away from adsorptive reactors, one can consider numerous other multifunctional catalyst pellets and other instances where an optimal distribution of process variables within the reactor is crucial for good reactor performance. The results of an extensive literature survey is summarised later in this chapter and serves as stimulation for the remaining work.

One can also combine multiple reactions, each catalysed by a different catalyst, in a single pellet to provide 'symbiotic' reaction conditions benefitting both the participating reactions. Chapter 4 addresses the possibility of pellet-scale thermal integration by combining an auxiliary exothermic reaction to drive an endothermic reversible reaction taking place on a separate catalyst. The catalytic dehydrogenation of ethylbenzene is employed as a test reaction scheme to study this pellet-scale thermal integration concept.

## **1.2. Literature survey**

The operating variables in a reactor are chosen to create favourable reaction conditions and achieve the desired process performance, which may be measured in terms of conversion, selectivity or any other suitable key process performance indicator (KPI). To arrive at the optimal reactor performance, different process variables must be tuned and often the optimal values of a process variable are not uniform, but function of pellet/reactor spatial coordinate or time. Though the distribution of some process variables may be intuitive, for others the solution is less obvious. This chapter is a compilation of the various works that has been carried out on distributing process variables within a reactor and serves as a background to the research done in this thesis.

### **1.2.1. Distribution within reactor space coordinate**

#### **1.2.1.1. Catalyst activity distribution**

The concept of distributing a single catalyst activity within a reactor space has been studied extensively. In the case of ethylene oxide synthesis in a multi-tubular fixed bed reactor, the highly exothermic nature of reaction results in the formation of temperature hotspots, which significantly lower process selectivity. Krishna & Sie [1994] report that a ramping of catalyst activity profile from the reactor entrance can significantly lower the formation of thermal hotspots and improve selectivity to the desired product.

In their pioneering work, Morbidelli et. al., [1982] showed that the optimal distribution of catalyst activity within a pellet depends on the reaction kinetics. However, to ensure an optimal overall reactor performance, the optimal activity distribution within a pellet alone is insufficient, and it is important to distribute these microstructured pellets optimally in the reactor space coordinate. It should be noted that in the case of single catalytic activity, the inert material acts as a diluent to achieve a suitable activity profile within the reactor and its inclusion lowers the space-time yield of the reactor.

The above examples illustrate the importance of activity distribution for a single catalytic activity. If activity distribution at the reactor level is of relevance for a single reaction, it is



even more important that activity distribution be considered as crucial optimisation variable for multiple functionalities within a reactor.

In the case of bifunctional catalysts, Gunn and Thomas carried out extensive studies on the distribution of the two catalyst activities within the reactor space. One can visualise a bifunctional catalyst as a multiple reaction system catalysed by two catalysts, where the second catalyst acts as a reactive mass sink and thus synergistically supports the primary catalyst to improve the overall process performance. Gunn and Thomas have shown that the distribution of the two catalyst functionalities is a function of both the reaction scheme under consideration and the reaction kinetics.

The concept of distribution of functionalities is also applicable to multifunctional reactors, especially adsorptive reactors and other solid phase functionalities. Adsorptive reactors are fixed-bed reactive separation processes in which selective removal (or addition) of a reaction species favourably modifies the concentration and temperature profiles within reactor to enhance process performance. Adsorptive reactors involve two distinct solid phase functionalities (catalyst and adsorbent) that need to be distributed optimally to provide the best reactor performance. The issue of activity distribution in the case of adsorptive reactors has been somewhat neglected. Most of the early reports on adsorptive reactors focussed on demonstrating the adsorptive reactor concept, but failed to even mention the amounts of catalyst and adsorbent used in the reactor. In the case of the Claus process, Elsner et. al., [2003] employed adsorptive reactors to increase conversion beyond equilibrium and showed the existence of an optimal catalyst to adsorbent ratio at which the process cycle time is significantly extended. Recently, Xiu et. al., [2003] proposed a varying catalyst to adsorbent ratio in the case of sorption enhanced steam reforming process.

While it is intuitively obvious that there is a need to distribute functionalities in the case of multifunctional reactors, the concept of distribution/profiling is less intuitive for other process parameters. The following discussion indicates importance of profiling for some other process parameters.

### **1.2.2. Residence time distribution in gas-solid reactors**

It is well-known from basic reaction engineering fundamentals that the degree of mixing is vital for controlling process selectivity and it is not uncommon that the mixing requirements for the participating reactants are different. Since the conventional co-fed mode of reactant feeding provides inadequate control for individually tailoring the residence time distribution of individual reactants, an expedient feeding strategy is essential. In contrast to the conventional co-fed mode, one could modify the residence time distribution by feeding the reactant(s) at distinct intermediate points along the reactor. The co-dimerisation of propene and butene to heptenes and chlorination of propene to allyl chloride are two instances where selectivity improvement has been achieved by feeding one of the reactants in this manner [Krishna and Sie, 1994]. Recently, Seidel-Morgenstern and his co-workers [Hamel et. al., 2003, Klose et. al., 2003] have adopted more complex dosing strategies in place of the co-fed mode to improve reaction selectivity towards an intermediate product of a complex series-parallel reaction system. As an alternative to discrete dosing positions along the reactor, the possibility of employing membranes for distributed reactant feeding through the reactor wall was analysed. This concept is applicable under favourable reaction order conditions and, for a sufficiently large number of membrane stages performance close to the optimal continuous dosing profile is attained.

### **1.2.3. Temperature profiling along the reactor coordinate**

As the sensitivities of chemical reactions to temperature are key characteristic of a reaction system, one can devise suitable temperature and heating/cooling profiles along the length of the reactor to encourage a favoured chemical reaction or suppress unwanted side reactions and thus enhance overall reactor performance. This technique is extensively used in microelectronic device manufacturing, where it is vital that wafers having uniform film deposits are produced. Low pressure chemical vapour deposition (LPCVD) techniques are used to process large number of wafers in a single batch,

yielding good film thickness and uniform composition. To achieve maximal film growth rate under the constraints of film uniformity, an axial temperature profile that increases along reactor length is commonly employed (Edgar, Himmelblau and Lasdon 2001).

With the recent emergence of hydrogen as an environmental-friendly alternative fuel, considerable effort has been devoted to exploiting sorption enhanced processes for hydrogen production. Recently, Xiu et al., [2003] studied the influence of temperature profile on the equilibrium shift in the sorption enhanced steam reforming process. For a reactor with uniform wall temperature, the concentration of steam reforming reaction by-products CO and CO<sub>2</sub> at the reactor outlet exceeds permissible limits prior to adsorbent exhaustion. This results in inefficient adsorbent utilisation and a shortened hydrogen production cycle. To overcome the above limitations, a wall temperature profiling along the reactor length offers more thermodynamically favourable conditions for the limitation of CO levels and thus permits a prolonged hydrogen production cycle with by-products below specified thresholds.

In addition to the concept of controlled temperature profiles along the reactor space coordinate, one can also contrive suitable reactor heating or cooling profiles along the reactor length. In the case of ethylene oxide synthesis, Krishna & Sie [1994] suggest that a controlled cooling profile along the reactor length would avoid temperature hot spots and improve the process selectivity towards ethylene oxide production, though they indicate that the catalyst dilution approach is simpler and would yield comparable performance.

#### **1.2.4. Pressure profiling within reactor**

It is well-known from Le Chatelier's principle that the extent of gas phase reversible reactions with a change in total mole number is sensitive to operating pressure. One can thus consider innovative reactor design concepts to establish favourable pressure profiles within the reactor in order to enhance process performance. Instead of conventional axial flow reactors, which offer a constant cross sectional area, radial flow reactors offer increasing or decreasing cross sectional areas and this can be exploited

advantageously for carrying out reversible reactions with increasing or decreasing mole numbers. One can also conceive a concave/convex pressure profile by changing the pellet size, but this inevitably entails the loss of catalyst effectiveness. As a result of work at Haldor Topsoe A/S, Denmark, this concept has been successfully commercialised and some important bulk chemicals like ammonia and styrene and UOP's Cyclar Process are now based on radial flow reactors. It should be noted that spherical reactors have also been developed to realise pressure profiling in reactors and one could envisage further innovative design level strategies to create favourable pressure profiles for enhancing process performance.

## **1.3. Distribution within pellet space coordinate**

The drive toward new energy efficient, low cost and zero waste chemical process technologies has inspired new research initiatives in catalysis. Proceeding from the early research work of Thiele, Wheeler and the like, considerable effort has been devoted to deepening the understanding of catalysis and the influence of transport phenomena on heterogeneous catalyst performance. These efforts have led to the evolution of catalysis from an art to a science and several books on catalyst design have already been published. In propounding a vision for further research in catalyst design and synthesis, Foley [1994] advocates structural uniformity and specificity of technical catalysts as being crucial to meeting future requirements. One can imagine different strategies for harnessing the porous pellet space to achieve an optimal catalyst performance. These strategies may be classified as follows:

- Inclusion of additional functionalities within the catalyst pellet
- Architecture of porous medium
- Mode of transport through the porous medium

### **1.3.1. Multiple functionalities within a catalyst pellet**

Though the era of multifunctional catalyst has only recently dawned in the field of reaction engineering, performance enhancement by synergistic integration of multiple functionalities is prevalent in nature and has been long known in the field of biochemistry. The motivation for integrating functionalities at a pellet level is to influence the concentration and temperature profiles favourably within the pellet and consequently at the reactor level.

Bifunctional catalysts are a common example of integrating multiple functionalities within a pellet. Weisz [1962] has carried out extensive studies on bifunctional catalysts. Gunn and Thomas investigated the effect of internal pore diffusion in bifunctional catalysts mathematically and confirmed the superiority of bifunctional catalysts over distinct catalyst activities localised in separate pellets. Recently, Agar and his co-workers

[Dissertation D. Hünemann, University of Dortmund, 2006] have studied the co-immobilisation of multiple enzymes within the same pellet. In all these cases, the second catalyst activity acts as a separate reactive functionality that alters the concentration profile favourably within the pellet to enhance catalyst performance.

Recently, Foley [1994] has developed a multifunctional catalyst using carbon molecular sieves (CMC) for methyl amine synthesis. Ammonia and methanol combine in a heterogeneously catalysed reaction to form primary, secondary and tertiary methylamines in a complex series of reversible reactions. Though thermodynamics favour the formation of tertiary methyl amines, the market demand for this amine is significantly lower than that for dimethyl amine. As catalysts have no influence on the thermodynamics of a chemical reaction, an innovative solution is required to resolve this problem. The introduction of a carbon molecular sieve layer around the pellet retains the tertiary amine within the pellets and the liberation of the other two amines from the pellet permits the re-conversion of this amine to primary and secondary amine by the reversible reaction.

In the present work, two interesting multifunctional catalyst concepts have been considered:

- integration of a catalyst activity and an adsorbent within the same pellet to yield an adsorptive catalyst pellet
- integration of an endothermic and exothermic reaction each catalysed by separate catalysts

In both the above cases, the presence of multiple functionalities within the pellet naturally raises the question of the appropriate distribution of the functionalities within the porous medium. With only limited knowledge of the underlying phenomena, one can propose a range of possibilities for distributing the functionalities within a pellet, ranging from a uniform distribution to complete segregation. Furthermore, as transport limitations within pellet are not always detrimental to process performance [Morbidelli et. al, 1982], it is necessary to take a systematic approach to the integration of functionalities at the pellet level. In this work, an attempt has been made to develop generic rules for the distribution of functionalities within pellet.

Apart from the above cases of multifunctional catalysts, there are a few examples of a second functionality being incorporated in the catalyst pellet for practical benefits. Such pellets may also be classified under the general heading of multifunctional catalysts. Heterogenisation of homogenous catalysts, immobilisation of enzymes, magnetised catalyst pellets [Krishna, 1994], VPO catalyst with an abrasion resistant silica shell [Contractor, 1987] are some examples of this type of multifunctional catalyst.

### **1.3.2. Porous medium architecture**

Proceeding from Wheeler's simplified representation of the porous medium as a network of idealised cylinders, significant improvements have been achieved in the description of the pore system complexity. More realistic 2D and 3D models, such as the parallel pore model and stochastic pore model have been developed which eliminate the need for 'fudge factors' like tortuosity. A compilation of the different approaches used to model porous medium is given by Keil [1999]. Gheorghiu and Coppens [2004], inspired by nature, recently proposed an optimal bimodal pore distribution, in which the arterial macropores form the transport highways for the reaction species to and from the high internal catalyst surface in nanopores using both fractal-like and uniform pore architecture. The relative ease in preparing fractal-like pore architecture leads them to endorse this design, even when the performance of both architectures is comparable. Recent developments in biomaterials such as templates and bacterial proteins for generating densely packed uniform nanostructures in catalysts indicate the growing possibilities for developing such structured catalysts [Hanisch, 2003].

### **1.3.3. Mode of transport through porous medium**

It is evident from the studies of Gheorghiu and Coppens [2004] that a monotonic pore dimension is a far from an optimal architecture and their work illustrates the superiority of bimodal pore architecture for the porous medium. In essence, if pore architecture is aimed to designing catalysts offering facile molecular transport without sacrificing the high catalyst internal surface area, one can also improve molecular mobility by selecting a particular mode of transport.

A common situation in reaction engineering is that of a multi-component mixture of reactants and products being transported through a porous catalyst matrix. The dusty gas model, based on the Maxwell-Stefan equations, reveals the different factors contributing to transport through a porous medium. Using simple momentum balance arguments, the model shows that mass transfer through a porous medium results from a combination of viscous and diffusive flux, the latter in turn is a sum of molecular and Knudsen diffusion mechanisms. In addition to these transport processes, thermal diffusion and transpiration may also contribute to the overall mass transfer process, but these contributions are usually small compared to the others and are often neglected.

In common industrial practice, the bulk of the molecular transport through porous catalyst medium occurs by diffusion. Occasionally, transport by diffusive flux alone is insufficient to ensure an effective utilisation of the entire catalyst activity. One approach to circumvent this shortcoming is to concentrate the catalyst activity at a specific location within pellet (in the catalyst shell or catalyst core). Though this approach results in a more effective catalyst activity utilisation, the concept suffers from inherently poor space-time-yield of the resultant reactors. An alternative technique for expediting the transport process would be to employ a convective mode of molecular transport. Birwa et al, [2004] and Khans et al. [2006] have extensively studied the interesting technique of “breathing catalysts” for enhancing the mass transport in diffusion-limited reactions without reducing the pellet size. A gas cushion established in the pore system of the catalyst support – preferably by the reaction itself – is periodically compressed and expanded by operating the reactor under oscillating pressure conditions. The resultant variation in the volume of the gas hold-up leads to a cyclic convective flow of liquid into and out of the pore system, which can dramatically exceed the rate of diffusive mass transfer arising in stagnant liquid-filled pores. The success of the concept is largely determined by the steady-state gas hold-ups within the porous medium. As capillary pressure is inversely related to the pore diameter, a large volume fraction of macropores is required to provide adequate gas hold-ups. This suggests that the performance of breathing catalysts could be improved by having a pore system with a greater fraction of macropores having diameters of 1  $\mu\text{m}$  or larger, which would serve



as the main repository of the gas cushion and the major arteries for convective mass transfer. This recommendation resembles the pore architecture of Georgiou and Coppers [2004] and demonstrates once again the intricate link between the transport process and pore architecture.

Datsevich [2003a, b] has carried out studies similar to the concept of breathing catalysts, except that he explored the natural oscillations arising within catalyst pores.

Diffusive transport within porous medium may also take place in the Knudsen regime. Though transport under Knudsen conditions is often employed in membrane separation processes, its low diffusion rates make it less desirable in catalyst operation. It should be noted that mass transport by surface diffusion and configurational diffusion, which is encountered in zeolites, are not discussed here.

## **Chapter 2: Structuring of adsorptive reactors at the reactor level**

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## **2.1. Introduction**

Adsorptive reactors are fixed-bed reactive separation processes that exploit regenerative storage capacity either to store selectively a specific component or heat and as a result enhance the process performance. Adsorptive reactors often exploit Le Chatlier's principle to displace equilibria and the adsorbent in the reactor may either serve as a mass or heat source/sink within the reactor. The selective addition or removal of mass/heat modifies the concentration and temperature profiles within the reactor. As the capacity of adsorbents is limited, they require periodic regeneration rendering the process inherently unsteady-state. The concept has attracted considerable attention as a hybrid process to enhance reaction selectivity and conversion for heterogeneously catalysed gas phase reactions and the modes of operation envisaged for an adsorptive reactor are described in the following sections.

### **2.1.1. Adsorbent as a mass source**

In this mode of operation, the adsorbent bed is pre-loaded with one of the reactants (adsorption cycle) and during the reaction cycle (desorption cycle) the reactant desorbs from the bed and selective reactant enrichment may affect the desired reaction favourably. Kodde et. al., [2000] have applied this concept to study reaction selectivity enhancement.

### **2.1.2. Adsorbent as a mass sink**

This is the most common mode of operation for adsorptive reactors. The adsorbent is employed to adsorb one of the by-products of a reversible reaction preferentially and the resulting favourable concentration profile drives the reaction forward. This concept can also be applied to selectivity problems. The Claus process [Elsner, 2004], steam reforming [Xiu et. al., 2003] and dehydrogenation reactions [Alpay et. al., 1994] are some of the instances in which adsorbents in an adsorptive reactor have been used as a mass sink.

### **2.1.3. Adsorbent as a heat sink**

Analogously to influencing chemical reactions by using adsorbents as mass source or sink, an adsorbent can also be employed as heat source or sink and create the appropriate thermal ambience for the desired reaction to occur. For example, an adsorbent can be pre-loaded with an inert material (or one of the reactants) during the adsorption cycle and during the reaction cycle (desorption cycle) the heat of reaction of an exothermic reaction is consumed by desorption of the inert, resulting in thermally balanced process operation. Richrath et. al., [2005] have employed adsorbents as heat sinks in their studies on 'desorptive' reactor cooling.

### **2.1.4. Adsorbent as a heat source**

Though it is more difficult to employ adsorbents as a heat source, one could employ the intensified regenerative heat storage capacity of phase change materials (PCMs) as a heat source or sink in adsorptive reactors. Maruoka et. al., [2004] have reported the possibility of using PCMs for heat recovery in the steel-making industry.

## 2.2. Literature review

The concept of adsorptive reactors has attracted considerable attention as a hybrid process to enhance reaction selectivity and conversion for heterogeneously catalysed gas phase reactions. An adsorbent acts as a selective mass source or sink for a particular reaction species (adsorbate) to create favourable concentration profiles within the reactor. Various reaction schemes have been studied experimentally and using numerical simulations to demonstrate the potential advantages of adsorptive reactors. Table 1 presents a summary of recent work that has been carried out on adsorptive reactors.

**Table 1: Compendium of recent publications on reaction schemes for adsorptive reactors**

Reaction scheme	Component adsorbed/ desorbed	Reference
$A + B \leftrightarrow C$	Either C or A & B is adsorbed	Arumugam et. al., 1998
Steam reforming of methane	Adsorption of CO <sub>2</sub> on potassium carbonate promoted hydrotalcite	Xiu et. al.,2003 Hufton et. al.,1999
Total isomerisation process (n-C <sub>5</sub> to i-C <sub>5</sub> )	Adsorption of n-C <sub>5</sub> on 5A zeolite	Al-Juhani., et. al.,2003
Claus process	Adsorption of H <sub>2</sub> O on 3A zeolite	Elsner, et al.,2002
HCN synthesis	Adsorption of CO <sub>2</sub> on LiZrO <sub>3</sub>	Elsner, et al.,2002
Dehydrogenation of methylcyclohexane	Clay based adsorbents	Alpay E., et. al.,1994
$A + D \rightarrow B + D \rightarrow C$	Desorption of reactant D	Kodde et. al.,1984

Several pioneering studies have been carried out to ascertain strategies for improving the performance of adsorptive reactors. For example, Yongsunthon and Alpay [1999] have studied the concept of feeding and withdrawing inlet and outlet streams at intermediate axial positions for a reaction taking place in a temperature swing reactor. They demonstrated that process performance may be improved by allowing intermediate feed introduction and product removal. The research group of Rodrigues (University of Porto, Portugal) has published many papers on methods to enhance the performance of adsorptive reactors based on their studies of the sorption-enhanced steam-reforming process. They have examined the possibility of reactive regeneration techniques [Xiu G.H., Rodrigues A.E, 2002] removal of a product stream from the middle of a pressure swing adsorptive (PSA) reactor [Lu Z. P., and Rodrigues A. E., 1994], and of temperature profiling and non-uniform catalyst/ adsorbent distribution along the reactor length to improve the utilisation of the adsorbent [Lee I.D., Kadlec R.H., 1984]

In addition to the strategies described above, attention has also been devoted to the appropriate distribution of the catalytic and adsorptive functionalities within an adsorptive reactor. For example, in the Claus process, an optimal uniform catalyst to zeolite adsorbent ratio is employed along the reactor length to maximise the breakthrough time of the reactant [Elsner, 2004]. For sorption enhanced steam-reforming, a reactor with three-subsections, each with a different ratio of adsorbent to catalyst has been employed to improve the reactor performance [Xiu et. al., 2003]. Though an improved performance is claimed, in conjunction with temperature profiling, little information is provided on the basis for choosing the different compositions and the design thus appears somewhat arbitrary. In both the above-mentioned publications, the distribution of the catalytic and adsorptive functionalities is such that finite quantities of both catalyst and adsorbent are present throughout the reactor. Recently though, a pressure swing adsorptive reactor process has been proposed for the isomerisation of n-paraffin [Al-Juhani., et. al.,2003], in which, in contrast to the previously mentioned work there is no overlap of the functionalities which are segregated into adjacent zones. As the n-paraffins adsorb more strongly than iso-paraffins, catalyst and adsorbent are employed in distinct beds and the reactor size is minimised by varying the individual bed lengths.

Thus a review of literature suggests that much effort has been devoted to identify the optimal distribution of catalyst and adsorbent within the reactor, but the results have been different for each case studied and general guidelines are lacking in this area. Though a few attempts have been made in this direction [Lee I.D., Kadlec R.H, 1984], so far the results seem inconclusive. The primary intention of this chapter is to fill these gaps and to develop some generally valid structuring guidelines. Detailed mathematical models of adsorptive reactors have been developed as part of this study to numerically analyse the performance of adsorptive reactors.

## **2.3. Mathematical modeling of adsorptive reactors**

Different modeling approaches of various degrees of complexity have been adopted in the past to analyse the performance of adsorptive reactors. Most of the early publications on this subject consider adsorption phenomena to attain local equilibrium instantaneously at a pellet level [Arumugam & Wankat, 1998, Alpay et. al., 1994]. It should be noted that like any heterogeneous gas-solid reaction system, adsorptive reactors are subject to mass and heat transport limitations and the above assumption is often invalid. As the mass transfer rate strongly influences the shape of the adsorption front (along with the adsorption isotherm), it is necessary to consider transport limitations in the modelling of adsorptive reactor.

Most of the recent work on adsorptive reactors have assumed a linear driving force (LDF) approximation to describe adsorption kinetics. The adsorption of CO<sub>2</sub> on hydrotalcite [Xiu et. al., 2003] and adsorption of H<sub>2</sub>O on zeolite 3A [Elsner 2004] are some of the cases where this approach has been adopted. As the LDF approach assumes a uniform concentration profile within the pellet, the approach is computationally very efficient.

As the purpose of this study is to analyse the effect of the distribution of functionalities, not just at a reactor level, but also on a pellet scale, the LDF approach is too simple to capture these effects and a more detailed approach is required. For this reason, a rigorous modelling of the behaviour of combined adsorption-catalyst pellets has been

adopted in obtaining quantitative predictions of adsorptive reactor performance in this study.

### **2.3.1. Model assumptions**

An unsteady-state heterogeneous two-phase dispersion model with internal pore diffusion describing the dynamic behaviour of a fixed-bed adsorptive reactor with separate catalyst and adsorbent phases has been developed. The model is based on the following simplifying assumptions. It is noted that some of the assumptions given are related to the reaction system considered in this study and hence their validity must be reassessed prior to the application in other reaction systems:

- the fluid in the pellet pores and the internal adsorbent/ catalyst surface are at equilibrium
- All sorbents possess a high surface area, and essentially the entire surface area is inside the pellet. The adsorptive gases contained in the “inert” carrier gas must penetrate into the porous structure during adsorption, and escape out of it during desorption.
- The mass flux in a porous medium is given by the sum of the following individual transport fluxes:
  - One of the following gaseous diffusion mechanisms dominates according to pore size
    - Molecular diffusion
    - Knudsen diffusion
  - Surface diffusion
  - Viscous flow
  - Transport due to thermal effects.

The contribution due to viscous flow and thermal effects is usually only slight and hence the flux due these phenomena is neglected.

Surface diffusion can be important for, and even dominate the total flux in the porous material, provided surface area and surface concentration are high. These



conditions are commonly met in adsorption processes and at times, the contribution of surface diffusion flux to the total flux could be as high as 40 to 80%. In this study, this effect has nevertheless been neglected and is assumed to be lumped in an effective diffusivity term. It should be noted that this effect has not been taken in to account in the previous work on adsorptive reactors as far as the author is aware. Thus in this model, the mass flux within the porous medium is assumed to occur by diffusion alone. The above macroporous diffusion model can be used to simulate transport flux in different commercial adsorbents like alumina, silica, activated carbon and molecular sieve carbons.

Zeolites are another class of commercial adsorbent where the diffusion is not governed by macropore diffusion, but by diffusion within the crystal nanopores. The model in its present form is not capable of modelling zeolite adsorption and needs to be extended to consider nanopore diffusion within zeolite crystal so that it can be applied for the simulation of zeolite adsorption processes.

- the adsorption process is assumed to be highly selective. This assumption is applicable to the test reaction scheme considered [Elsner, 2004]. It should be noted that this assumption is not always realistic for physisorption processes, but is probably reasonable for chemisorption processes.
- the physical structure of the pellets can be idealised as porous spheres with a uniform pore structure
- pellet size and structure can be averaged for all pellets in order to permit a direct comparison of different pellet and reactor configurations
- backmixing in bulk fluid phase flow is lumped into an axial dispersion coefficient term
- the gas phase behaviour obeys the ideal gas law
- heat effects are neglected and the reactor is operated isothermally
- the volume change due to reaction is neglected. This is justified due to the high dilution of the reaction systems considered with 85% inert.
- the bed is assumed to be free of any adsorbate at the start of the adsorption cycle.

## 2.3.2. Reactor model

The pellet models are incorporated in a fixed-bed reactor and one-dimensional axial dispersion model, which is used to describe the reactor fluid bulk phase is shown below. The third term on the right hand side of accounts for the mass transfer from the fluid bulk phase to the catalyst and adsorbent pellet, each weighted according to the contribution of the volume fractions of the pellets in the fixed-bed.

$$\varepsilon \cdot \frac{\partial c_i}{\partial t} = -u \frac{\partial c_i}{\partial x} + D_{ax} \cdot \varepsilon \cdot \frac{\partial^2 c_i}{\partial x^2} - (1 - \varepsilon) \cdot \frac{3}{R_p} \cdot \left( f_{ads} \cdot k_{film} \left( c_i - c_{p,ads,i} \Big|_{R_p} \right) + f_{cat} \cdot k_{film} \left( c_i - c_{p,cat,i} \Big|_{R_p} \right) \right) \quad \text{Equation 1}$$

Here,  $f_{ads}$  and  $f_{cat}$  are function of the axial position along the reactor. The reactor boundary conditions have been chosen assuming closed vessel behaviour.

$$u \cdot \left( c_i(x=0, t) - c_{0,i} \right) = D_{ax} \cdot \frac{\partial c_i(x=0, t)}{\partial x} \quad \text{Equation 2}$$

$$\frac{\partial c_i(x=L, t)}{\partial x} = 0 \quad \text{Equation 3}$$

## 2.3.3. Pellet model

Inside the pellets, the mass transfer is described using an effective pore diffusion model and the following expression gives the mass balance for the adsorbent and catalyst pellet.

$$\varepsilon_p \frac{\partial c_{p,i}}{\partial t} = D_{eff,i} \left( \frac{\partial c_{p,i}}{\partial r} \cdot \frac{2}{r} + \frac{\partial^2 c_{p,i}}{\partial r^2} \right) - (1 - \varepsilon_p) \cdot r_{Vads,i} \quad \text{Equation 4}$$

In the above expression,  $r_{V_{ads,i}}$  represents the rate of adsorption at any location within the pellet. For any non-adsorbing species,  $r_{V_{ads,i}} = 0$  and only transport by diffusion occurs within the pellet.

The mass balance for catalyst pellet is given by the following expression:

$$\varepsilon_p \frac{\partial c_{p,i}}{\partial t} = D_{eff,i} \left( \frac{\partial c_{p,i}}{\partial r} \cdot \frac{2}{r} + \frac{\partial^2 c_{p,i}}{\partial r^2} \right) - (1 - \varepsilon_p) \cdot r_{V_{cat,i}} \quad \text{Equation 5}$$

The boundary conditions for the pellet mass balance are obtained by assuming linear concentration profiles at the outer pellet boundary layer and symmetric profiles within the pellets.

$$k_{film,i} \left( c_i - c_{p,i} \Big|_{r=R_p} \right) = D_{eff,i} \frac{\partial c_{p,i}}{\partial r} \Big|_{r=R_p} \quad \text{Equation 6}$$

$$\frac{\partial c_{p,i}}{\partial r} \Big|_{r=0} = 0 \quad \text{Equation 7}$$

At the outset of each adsorption cycle, the reactor only contains just an inert component i.e.

$$c_i(x, t = 0) = 0, c_{p,i}(r, t = 0) = 0 \text{ for all } i \neq \text{inert} \quad \text{Equation 8}$$

$$c_i(x, t = 0) = c_{0,inert}, c_{p,i}(r, t = 0) = c_{0,inert}, i = \text{inert} \quad \text{Equation 9}$$

## **2.4. Numerical solution**

From the previous section it is clear that the performance of an adsorptive reactor can be described using a set of partial differential and algebraic equations and any good equation-based solver may be used to find the numerical solution. Of the various commercially available software, gPROMS<sup>®</sup> (Process Systems Enterprise Ltd) and Aspen Custom Modeler<sup>®</sup> (AspenTech Ltd) are some of the best-known equation-based solvers available. In this work the model has been implemented in Aspen Custom Modeller with a modular model structure and then solved using the method of lines. The spatial domain has been discretised using backward finite difference method with 100 finite elements for the reactor length axis and on 28 elements over the pellet dimension, with the central finite difference on the radial axis of the pellet being allocated in such a manner as to obtain an equivalent volume increment grid. This procedure ensured a better numerical resolution of the pellet mass balances by employing incremental control volumes of equal size.

### **2.4.1. Optimisation problem description**

Any study on the performance of an adsorptive reactor is deemed complete if and only if both the adsorption and desorption steps of an adsorptive reactor are taken into consideration for the performance analysis. It is known from standard works on adsorption processes [Yang, 1997], that more than one method is available for regeneration and, very often, a combination of different methods is required for an efficient and complete desorption. In addition to the well-known non-reactive desorption techniques, reactive desorption techniques have also been suggested [Xiu et. al., 2002] to improve the desorption performance of an adsorptive reactor and one thus has numerous options at ones disposal. The choice of a particular regeneration strategy for an overall optimisation study to develop the proposed structuring guidelines would have therefore introduced an arbitrary element into the analysis. Furthermore, as any catalyst in an adsorptive reactor acts merely as an inert during the desorption step (unless the

catalyst possesses strong adsorbing properties towards the adsorbate or under reactive desorption conditions), the inclusion of the desorption step is not expected to alter the results presented in this chapter significantly and for this reason, the optimisation studies are limited to the adsorption cycle alone.

To compute the optimal catalyst/adsorbent distribution in an adsorptive reactor, the optimisation space is subdivided into discrete sections and the optimal value is calculated for each discrete section (Figure 1). Though it might be more desirable to obtain a continuous optimal activity distribution profile along the reactor length, the problem is simplified by this discrete approach, which was found to be entirely adequate. It should be noted that comparable studies on catalyst dilution for smoothing reactor temperature profiles have revealed only modest sensitivities for influence of the precise fixed-bed structure on the performance. In this study, the reactor has been divided up into 13 discrete sections. Within any discrete element, the catalyst fraction is the decision variable that is optimised to maximise the reactor performance. The definition of the optimisation is thus as follows:

Objective Function	Max. Cycle time, $\tau$
Decision variables	Catalyst fraction in any discrete $f(x)_{cat,i}$ $i = 1, 2, \dots$ no. of segments
Process constraints	$0 < f_{cat,i} < 1$ $f_{cat,i} + f_{ads,i} = 1$ Conversion $X(t) >$ Desired minimum conversion $X_{min}$

For any given reactor volume, feed flow rate conditions and desired minimum conversion, the process cycle time is a direct measure of the extent of the adsorbent utilisation and thus deemed to be an appropriate optimisation criterion for the process.

As mentioned earlier, dynamic simulation and optimisation studies have been carried out using Aspen Custom Modeler (ACM). The successive quadratic programming optimiser,

FEASOPT<sup>®</sup>, which is part of the ACM, was used to carry out dynamic optimisation. FEASOPT employs a reduced space optimisation method to arrive at the optimal solution. It evaluates the objective function (cycle time) at the current point and adjusts the decision variables (catalyst fraction values) to take the objective function towards its optimum value. After solving with the new values of the decision variables, FEASOPT re-evaluates the objective function. In this way, it converges iteratively towards the optimum solution. FEASOPT solves the simulation at each step subject to simulation equations, variable bounds and any other constraints applied to the optimization.

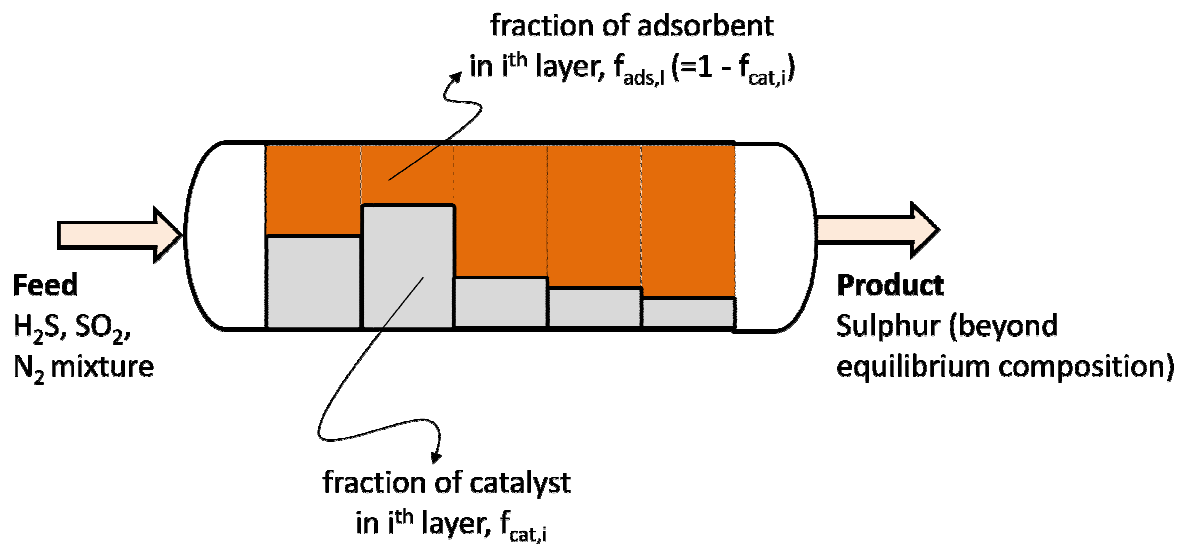
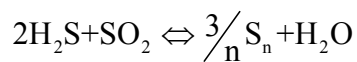


Figure 1: Scheme for the optimal distribution of functionalities in adsorptive reactor at a reactor level.

## 2.5. Model reaction system

The single stage CLAUS process, an adsorptive reactor concept proposed previously [Elsner, Dittrich, Agar, 2002] by our group, has been chosen as a reference system for this study. The Claus process involves the conversion of sour gases ( $H_2S$  and  $SO_2$ ) into elemental sulfur and water by a reversible chemical reaction. In this case, adsorption of the by-product  $H_2O$  results in conversion enhancement of the equilibrium reaction according to Le Chatelier's principle. The reaction kinetics over an  $\gamma$ - $Al_2O_3$ -catalyst has been described with the simple power law expression given below:



Here,  $n \approx 8$

$$r_{V,i} = v_i \cdot k_1 \left( p_{H_2S}^{0.95} \cdot p_{SO_2}^{0.22} - \frac{p_{H_2O}^{0.99}}{K_{eq}} \right) \frac{\text{mmol}}{\text{s kg}_{\text{cat}}} \quad \text{Equation 10}$$

where  $K_{eq} = \frac{k_1}{k_2}$  is the reaction equilibrium constant.

The water vapour formed is adsorbed on a 3A zeolite with the adsorption equilibrium being described using a Freundlich-type isotherm [Elsner, 2004].

$$q_{H_2O} = K_{F,H_2O} \cdot c_{H_2O}^{0.75} \quad \text{Equation 11}$$

The model parameters required have been obtained from literature data [Elsner, 2004] or calculated using empirical correlations and are summarised in Table 2. As our interest in this work is to develop generic guidelines for the distribution of catalyst and adsorbent pellets, we have used the Claus kinetics as the base case and extended the study by varying the kinetic parameters ( $k_1$  &  $k_2$ ) and other process parameters. Table 3 indicates the various combinations of kinetic parameters used in this work.

Figure 2 shows the effect of pellet diameter on Thiele modulus ( $\phi$ ) for the Claus reaction at reactor inlet conditions. The low Thiele modulus values suggest that the reaction kinetics are not particularly fast. Considering the reaction kinetics and high reaction

equilibrium values for Claus process (equilibrium conversion is 96.9%), additional case studies have been chosen such that the reaction schemes have high  $k_1$  values (fast reaction rate) and appropriate  $k_2$  values such that  $K_{eq}$  is somewhat lower (low equilibrium conversion).

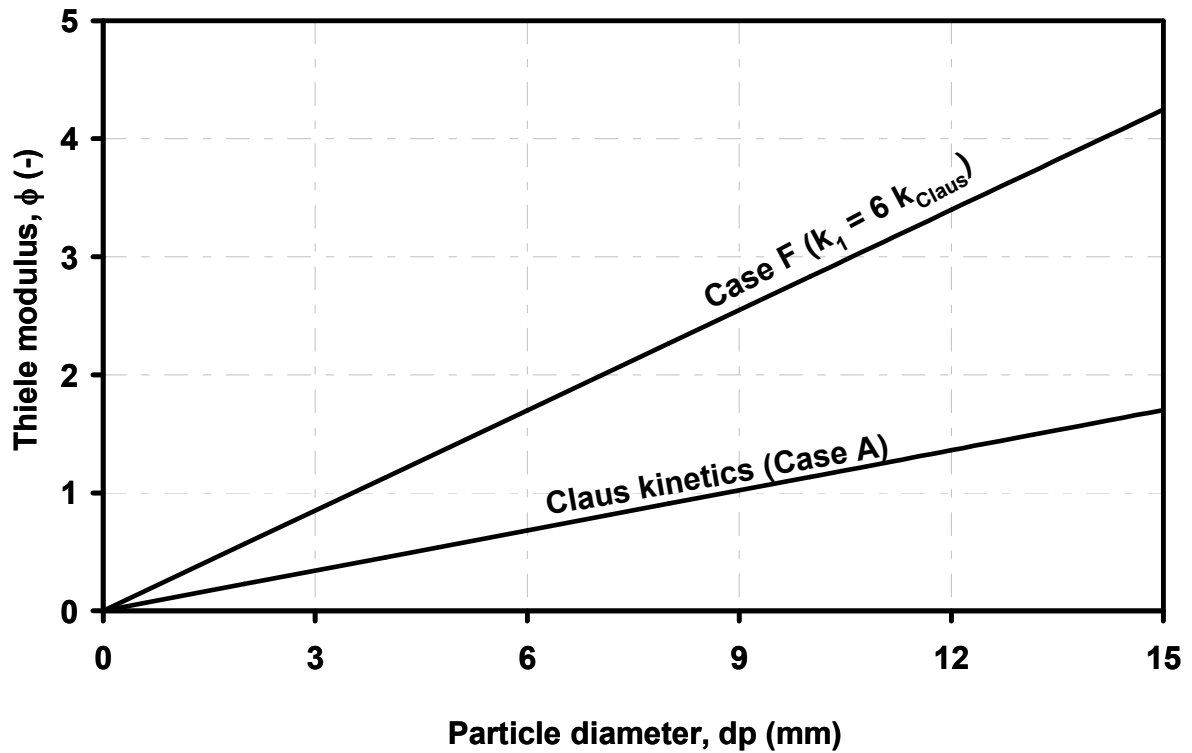


Figure 2: Variation of Thiele modulus with pellet diameter at reactor entrance conditions for constant diffusivity



**Table 2: Combination of rate constants and equilibrium constants for different data sets analysed in this study**

Case	$k_1, \frac{\text{mmol}}{\text{s kg}_{\text{cat}} \text{mbar}^{1.17}}$	$k_2, \frac{\text{mmol}}{\text{s kg}_{\text{cat}} \text{mbar}^{0.99}}$	$K_{\text{eq}}, \text{mbar}^{-0.18}$	Equilibrium conversion, $X_{\text{eq}}$
<b>A (Claus)</b>	0.0303	0.0010	29.28	96.9 %
<b>B</b>	0.0309	0.5957	0.052	8.9 %
<b>C</b>	0.0303	0.0484	0.626	51.7 %
<b>D</b>	0.0113	0.0484	0.234	29.4 %
<b>E</b>	0.0845	0.0177	4.76	86.8 %
<b>F</b>	0.1888	0.1321	1.429	69.4 %

**Table 3: Model parameters and correlations used in the case study**

Component	Inlet composition		
$p_{\text{H}_2\text{S}}$	0.1 bar		
$p_{\text{SO}_2}$	0.05 bar		
$p_{\text{N}_2}$	0.85 bar		
$\varepsilon$	0.4	T	250 °C
$\varepsilon_p$	0.5	P	1.013 bar
$D_i$	$5.55 \times 10^{-5} \text{ m}^2/\text{s}$	$d_p$	2 – 8 mm
L	1.5 m	D	0.06 m
u	0.15 - 0.35 m/s	$k_{\text{film}}$ & $D_{\text{ax}}$	Wakao, Funazkri [1978]

## 2.6. Results and discussion

Since the primary aim of this chapter is to demonstrate the importance of the distribution of catalyst and adsorbent pellets in an adsorptive reactor, we shall deal with the process architecture at three different levels:

- A constant fraction of catalyst and adsorbent (uniform distribution) at every location in reactor. Here, the catalyst and adsorbent are present in separate pellets (conventional adsorptive reactor). This is termed homogenous axial distribution.
- A variable fraction of catalyst and adsorbent (non-uniform distribution) at every location in reactor. Here again, the catalyst and adsorbent are present in separate pellets (conventional adsorptive reactor). This is termed a macrostructured distribution.
- A combination of catalyst and adsorbent within the same pellet is referred to as micro-integrated pellets. A macrostructured distribution of micro-integrated pellets can be envisaged, as can the microstructuring of the adsorptive and catalytic functionalities within the pellet.

In this chapter, we shall confine our discussions to the first two levels alone. The third level will be the subject of discussion in Chapter 3. We shall use one of the test cases (Case-E) to study the performance improvements that may be achieved by carrying out structuring at different levels. The following discussion is based on the following operating point. ( $X_{equ} = 86.8\%$ ,  $u = 0.3$  m/s,  $d_p = 2$ mm,  $X_{min} = 96\%$ )

### 2.6.1. Level 1: Homogenous axial distribution of catalyst and adsorbent pellets

This is the simplest method of distributing catalyst and adsorbent within a reactor. The catalyst and adsorbent are present in separate pellets and the same volume fraction of catalyst (and adsorbent) is present at every location in reactor. Though the objective

function of the optimisation can be varied, it is defined here as the optimal catalyst fraction, which for the minimum conversion level desired, offers the longest cycle time. Figure 3 shows the existence of such an optimal catalyst fraction in this test case. Essentially, when too little catalyst is present in the reactor, the reaction ceases to occur resulting in the early breakthrough of the reactants and a low cycle time. On the other hand, when the catalyst fraction is too high, the reaction approaches reaction equilibrium, but as the adsorbent fraction is too low, the conversion quickly drops back to the equilibrium value upon adsorbent saturation. By choosing the optimal ratio, we strike a balance between breakthrough of reactant due to lack of reaction beyond equilibrium because of absence of adsorbent (right of the optimal point in figure below) or too little reaction (left of the optimal point).

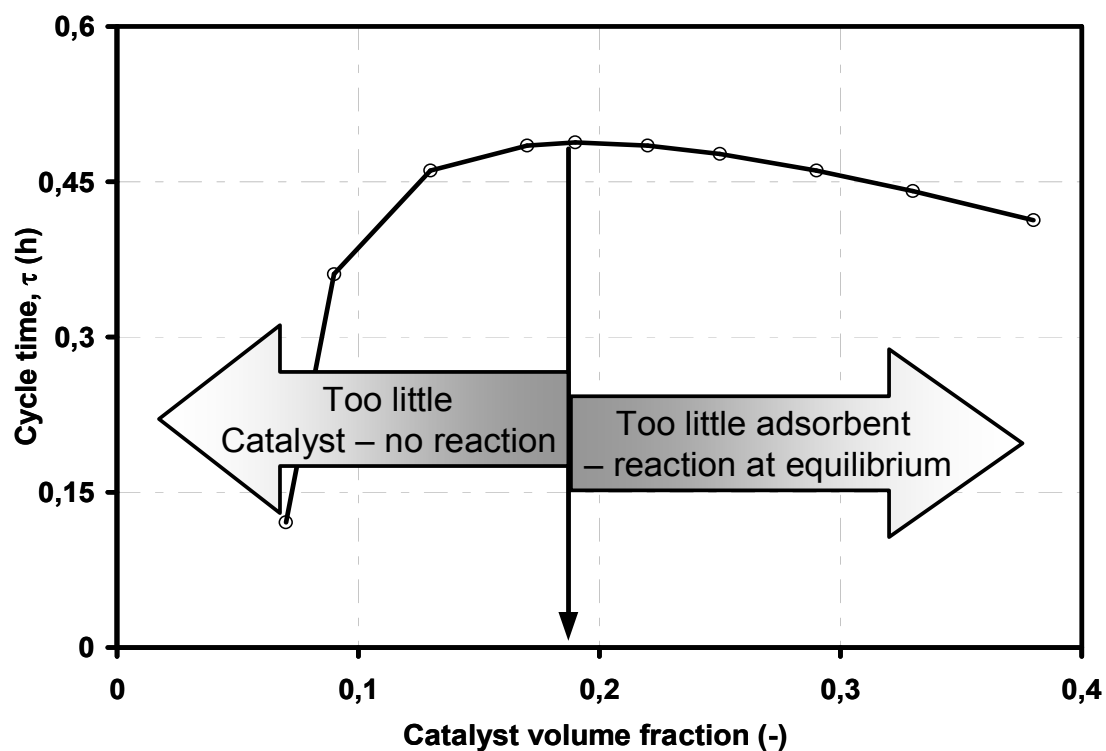


Figure 3: Influence of catalyst volume fraction on process cycle time under homogenous distribution condition

Since the homogenous distribution is deemed to be the simplest of the structuring approaches, we shall take this optimal cycle time to be the benchmark value and compare the performance obtained at the next level against this result.

## 2.6.2. Level 2: Non-uniform axial distribution

At the previous level, though the choice of the optimal value offers the longest possible cycle time, the results provide very little indication as to the utilisation of the catalyst and adsorbent functionalities. Any tool that might indicate the extent of utilisation of functionalities may help us ascertain the truly optimal nature of the result. One approach to indicate their utilisation is to use the approach to equilibrium parameter ( $\Lambda$ ) a direct measure of the reaction driving force at any spatial location within reactor defined by,

$$\Lambda = \frac{\prod_i c_i^{v_i}}{K_{eq}} = \frac{p_{H_2O}^{0.99} k_2}{p_{H_2S}^{0.95} p_{SO_2}^{0.22} k_1} \quad \text{Equation 12}$$

If  $\Lambda = 1$ , the reaction is at thermodynamic equilibrium

$\Lambda > 1$ , forward reaction occurs

$\Lambda < 1$ , backward reaction occurs

Figure 4 shows the variation of the approach to equilibrium parameter for the test case at its optimal homogenous distribution for different process times prior to breaching the process constraint. This graph is typical for any reversible reaction taking place in an adsorptive reactor. To obtain useful information from the variation of  $\Lambda$  in the reactor, the reactor is divided in to 3 segments and each segment analysed separately.

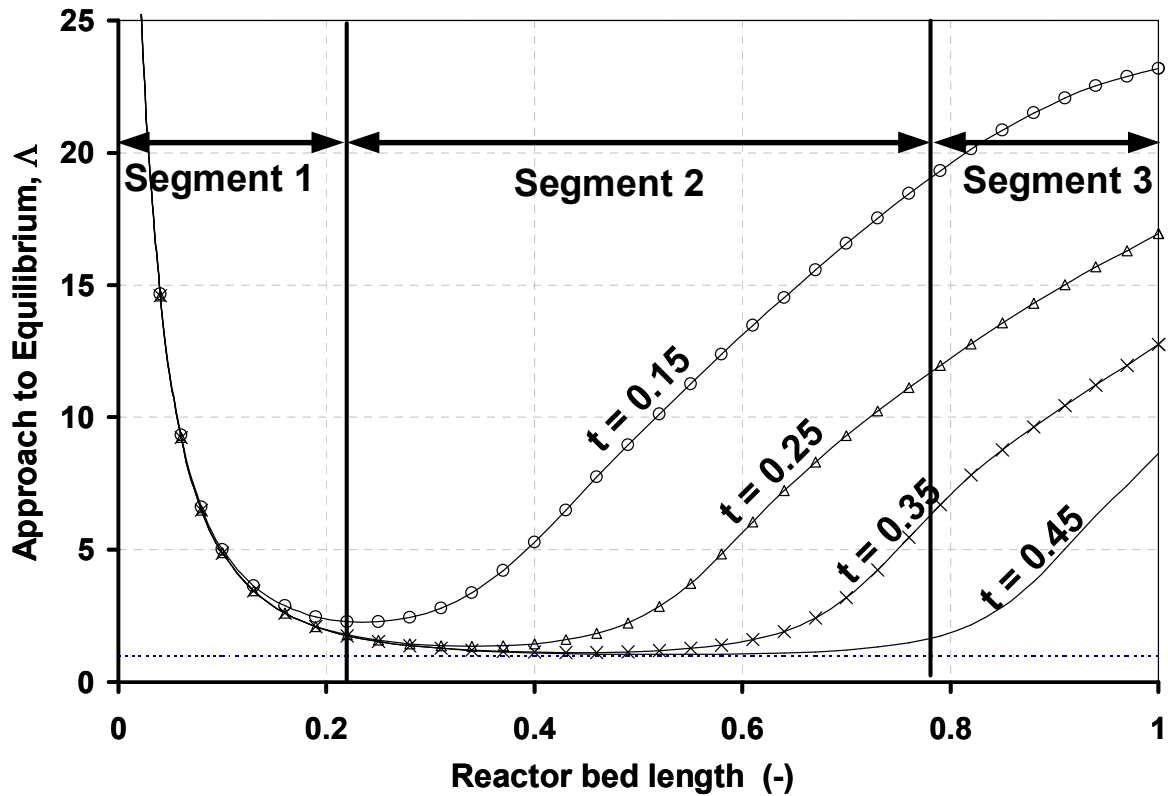


Figure 4: Variation of approach to equilibrium along the axial space at different process time for the test case

### 2.6.2.1. Segment 1

In this segment, the value of  $\Delta$  is always greater than one and is virtually a constant with time. The meagre product concentration in this segment exerts a negligible influence on the reaction rate and the segment is always kinetically controlled. Thus any adsorbent present in this segment plays only a passive role in its performance.

### 2.6.2.2. Segment 2

In this segment, the value of  $\Delta$  is a function of position and time. At any point, as long as the adsorbent is unsaturated, the forward chemical reaction occurs and  $\Delta$  is greater than one. Once the value of  $\Delta$  reaches one, the potential to adsorb ceases and the reaction is no longer pushed beyond equilibrium any longer. Thus, Figure 4 suggests that though the zone is kinetically governed initially, the imposition of the sorption regime renders any catalyst present in this segment ineffective. This ineffective utilisation of the catalyst strengthens the case against the global nature of the optimal homogenous axial distribution results.

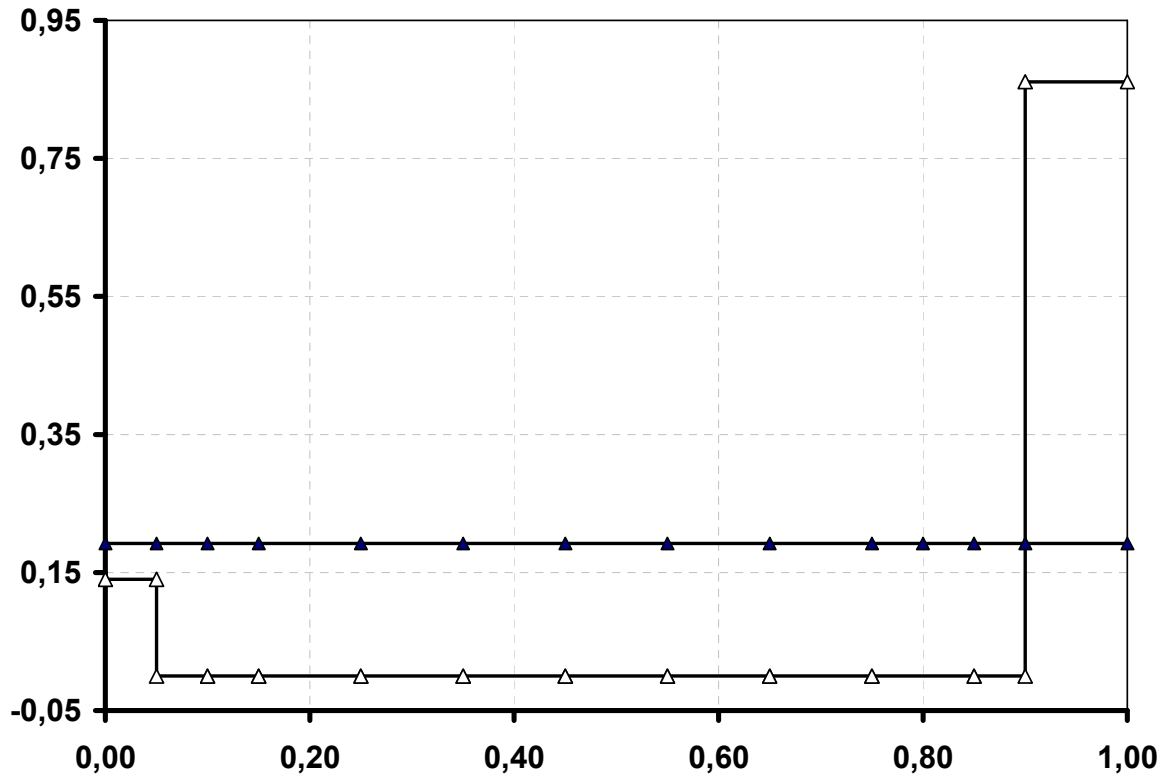


Figure 5: Comparison of the optimal catalyst functionality distribution in the case of homogeneously distributed adsorptive reactor (filled points) and the optimally macrostructured adsorptive reactor

### 2.6.2.3. Segment 3

The behaviour of this segment is similar to segment-2 and may be considered as its extension. What distinguishes these two segments is that, unlike segment-2, the adsorbent in section-3 remains unsaturated, even up to the point at which the process constraint is breached. Hence, this section is kinetically controlled throughout the process cycle.

The existence of the third segment is attributable to the minimum conversion constraint imposed on the process, but such a constraint is a logical criterion for industrial applications. For example, in the Claus process, the desired conversion is determined by environmental legislation [for example, TA Luft, 1986] which typically demands a minimum sulfur recovery of 99.5%. Similarly, in the case of hydrogen production for fuel cells by sorption enhanced steam reforming process, Xiu et al. [2003] impose a minimum methane conversion of 50%.

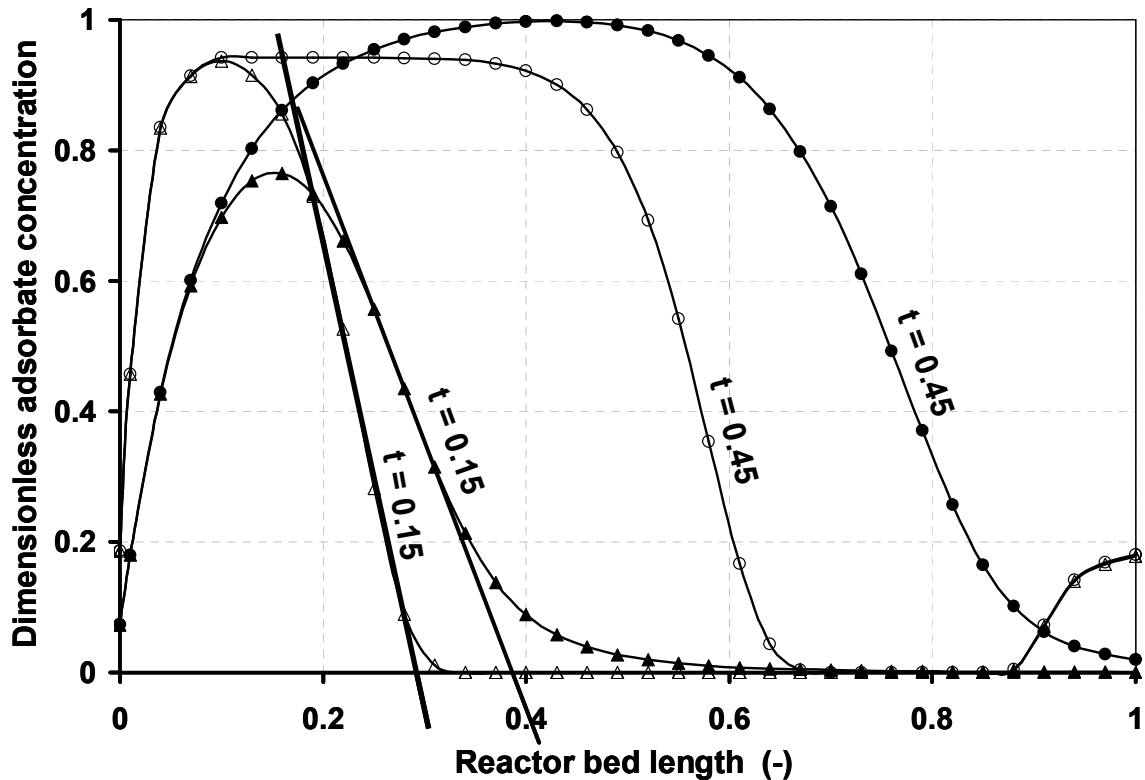


Figure 6: Comparison of progression of adsorbate concentration fronts in a macrostructured adsorptive reactor and homogeneously distributed adsorptive reactor. The filled data points correspond to the homogenous distribution case and the empty ones correspond to the macrostructured adsorptive reactor

It is thus clear from the previous discussion that, at any time, different regimes govern an adsorptive reactor and this leads one to question the true optimal nature of the results from the homogenous distribution studies (Level-1). This warrants a macrostructuring optimisation study, where the catalyst and adsorbent pellets are distributed non-uniformly along the reactor.

To carry out this level-2 optimisation study, the reactor is divided into discrete segments and catalyst fraction in each segment is a decision variable, which is adjusted by the optimiser to arrive at the optimal value of the objective function (maximise process cycle time). Figure 5 shows the non-uniform distribution derived for the test case discussed. The result depicts a distribution in which a pure layer of adsorbent is sandwiched between layers of catalyst at the reactor entrance and exit, corresponding to the presence of kinetic regimes at these locations, and an intermediate sorption regime between them, strongly reflecting the conclusions drawn from the approach to equilibrium study (Figure 4). This optimal distribution of catalyst and adsorbents yields an

increase in the process cycle time over the homogenous distribution (level-1). The improvement in process cycle time over homogenous distribution is significant and may be as high as 150%. It should be noted that this performance gain is dependent on the desired minimum conversion, an aspect which will be discussed later.

As indicated earlier, the enhancement of the performance may be attributed to a more effective allocation of catalyst and adsorbent within the reactor. For the test case, in which the desired minimum conversion is set to 96%, macrostructuring results in a 30% reduction in the catalyst requirements over the uniform axial distribution case. Though this reduction in the catalyst amount may appear significant, owing to its low absolute value (from 0.19 to 0.14 volume fraction of bed), this would correspond to only a 6% increase in the adsorbent volume in the reactor bed. This marginal increase in adsorbent volume does not allow one to claim that performance improvement by macrostructuring is due to an increase in the adsorbent volume in the reactor. The progression of the adsorbate concentration fronts provides a more plausible explanation for the differences in performance.

It is known from standard works on adsorption [for example, Yang, 1997] that the shape of an adsorbate concentration front is primarily governed by the sorption isotherm and to a lesser extent by the transport limitations and axial dispersion in an absorber bed. Hydrodynamic irregularities and mass transfer resistances tend to widen the adsorbate concentration front and hence, accelerate front breakthrough. In the case of a non-uniform distribution (Figure 5), the adsorbent section is essentially de-coupled from the catalyst beds and its performance is governed only by adsorption separation principles. Under homogenous distribution conditions, there is a simultaneous formation of adsorbate in segment-1 and segment-2. Though the reaction occurring in segment-2 is much less than that in segment-1, it influences the adsorbate concentration front in a fashion similar to transport resistances, resulting in a widening of the front culminating in a premature front breakthrough. Figure 6 compares the development of adsorbate concentration fronts in the two cases. This analysis confirms that the process improvement by macrostructuring is not due to the increase of adsorbent volume in bed, but rather due to the more effective utilisation of individual functionalities.



It is thus obvious that macrostructuring of adsorptive reactors is crucial for its optimal performance. As a result of structuring, the adsorbent is well-utilised without any additional complication in the reactor design. So far, we have demonstrated the impact of structuring using a test case. Now, in order to generalise the results of this study, we will present similar structuring studies for different combinations of kinetic parameters, under different desired minimum process conversion constraints and process parameters. Figure 7 shows the influence of structuring an adsorptive reactor for different equilibrium constants. The continuous solid line shows the variation of equilibrium conversion against the reaction equilibrium constant for the given reaction kinetics (Equation 10). For any desired conversion below the equilibrium line, there is little justification for employing an adsorptive reactor and a conventional heterogeneously catalysed gas phase reactor is entirely adequate. The data points correspond to the case studies that have been studied and the adjoining numbers indicate the increase in the performance for a macrostructured adsorptive reactor over homogeneously distributed adsorptive reactor.

## 2.7. Optimal macrostructure – alternate catalyst and adsorbent layers?

It is interesting to note that structuring has the potential to enhance the process performance in excess of 100% over optimised uniformly distributed adsorptive reactor, when desired conversions are close to reaction equilibrium values (Figure 7), while it loses its relevance as more stringent conversion demands are set. For a low desired minimum conversion, a macrostructured reactor resembles a reactor-in-series arrangement, with an adsorber bed sandwiched between two catalyst beds. The volume of these catalyst beds are dictated by the reaction kinetics and mass transport limitations of the system. The total volume of the catalyst is divided between the two beds and it is known from the approach to equilibrium studies that the catalyst is divided such that the beds are kinetically controlled throughout the process (refer Figure 8 and related discussions).

So far, we have demonstrated that macrostructuring results in an asymptotic reactor-in-series arrangement where an adsorbent bed is sandwiched between two catalyst beds. From one point of view, this optimal macrostructure is nothing more than the simplest arrangement of alternative layers of catalyst and adsorbent in a reactor. At this juncture, the natural question that arises, is whether multiple alternating layers of catalyst and adsorbent would always yield an optimal solution to the problem of macrostructuring.

The following analysis provides an answer to this question and designates the conditions under which such a structure is appropriate. To explain this phenomenon, we shall take the results from the test case-D, where the reaction equilibrium constant is fairly low ( $K_{eq} = 0.23$ ) limiting the equilibrium conversion to 29.4%. A non-uniform distribution of catalyst and adsorbents results in an improvement in performance up to a desired minimum conversion of around 75%. Beyond this conversion, the macrostructuring loses its efficacy and a macrostructured distribution performs just as well as a homogenous distribution (Figure 9).

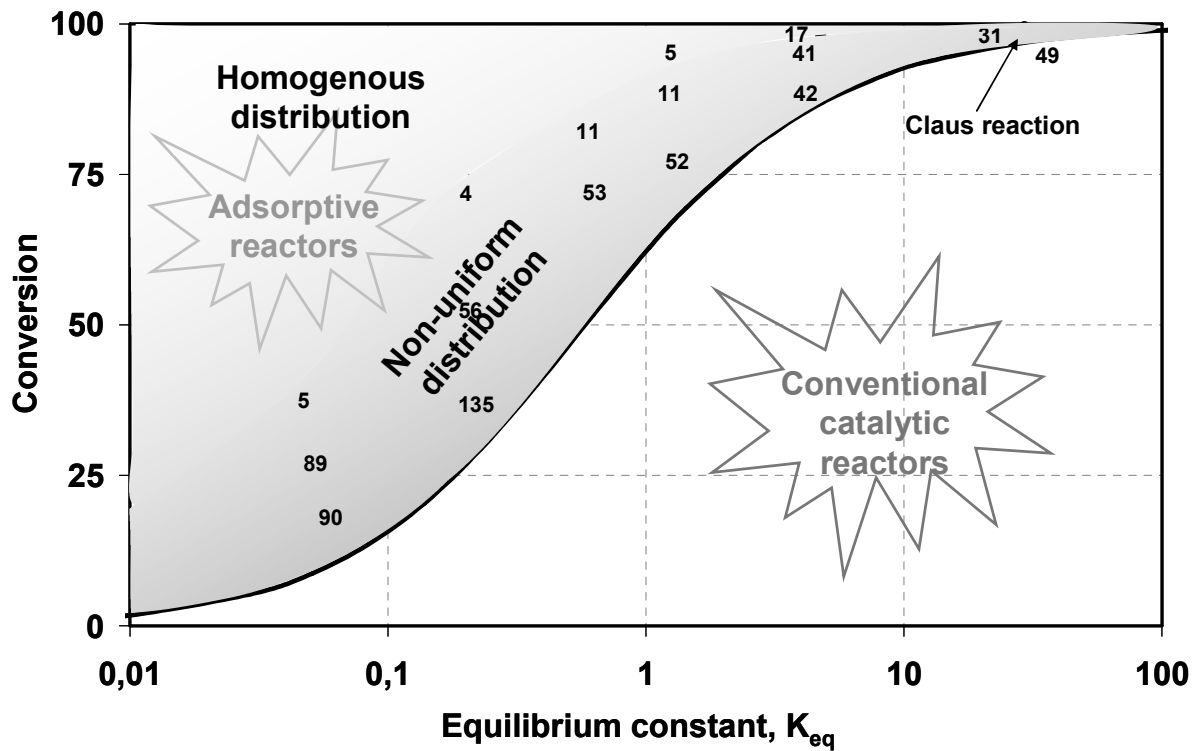


Figure 7: Influence of structuring on the performance of an adsorptive reactor for different values of reaction equilibrium constant. The numbers indicate the percentage increase in performance of macrostructured adsorptive reactor over homogeneously distributed adsorptive catalyst

For a desired conversion of 40%, the optimal non-uniform distribution is found to be reactor-in-series arrangement, where a single adsorbent bed is sandwiched between two catalyst beds. As the desired minimum conversion is increased to 55%, a non-uniform distribution is still found to be the optimal distribution. However, the more stringent process constraints demand a higher volume of catalyst and the two catalyst bed distribution can no longer be structured such that they both operate under kinetically controlled regimes throughout the process cycle. This constrains the optimiser to distribute the catalyst in more than two beds. For the case of 55% desired conversion, the optimiser assigns the distribution of catalyst into three beds with two adsorbent beds sandwiched between them (Figure 9) illustrates the development of the adsorbate concentration front when the desired conversion is set to 55%. The reactor space before and after the second catalyst bed are saturated simultaneously by the adsorbate produced in catalyst beds 1 and 2 resulting in an efficient adsorbent utilisation. On further increase in the desired conversion to 75%, a macrostructured distribution tends towards a homogenous distribution with comparable performance.

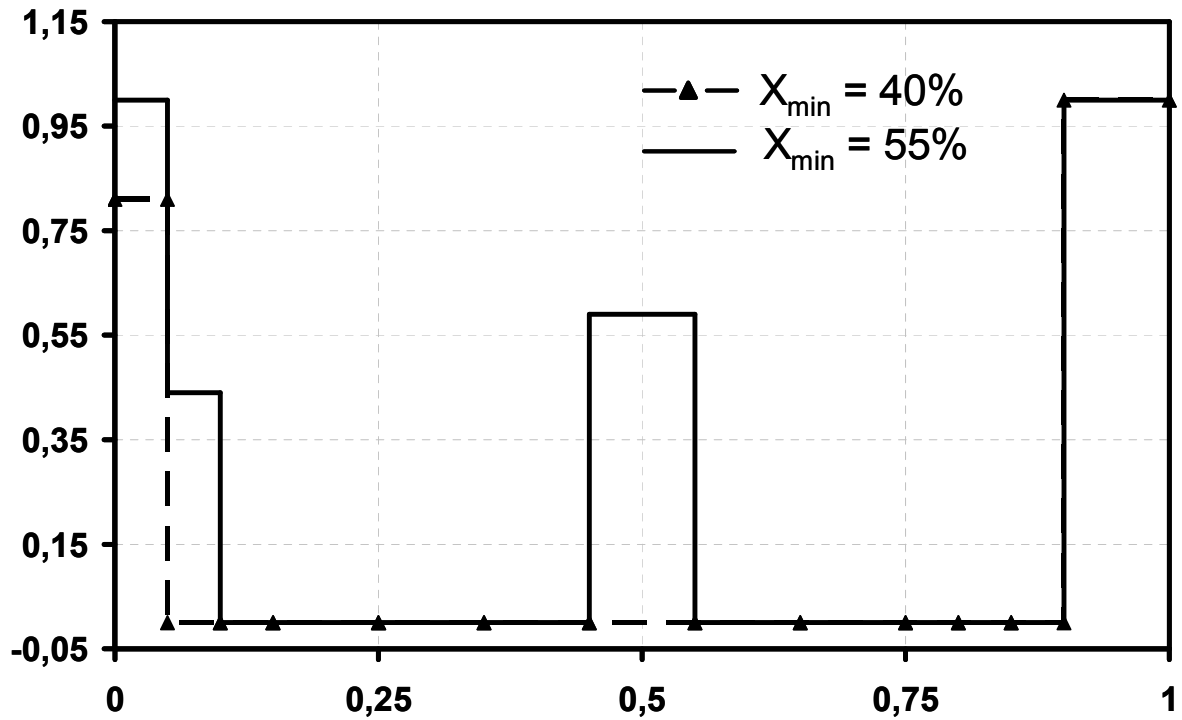


Figure 8: Effect of minimum conversion on the optimal macrostructure for the case,  $k_1 = 0.447$  and  $K_{eq} = 0.23$

It should be noted here that this multiple alternate catalyst and adsorbent beds are found to be optimal only for low equilibrium constant values (typically less than one) and at high reaction equilibrium constant values, this gradual transition is less conspicuous.

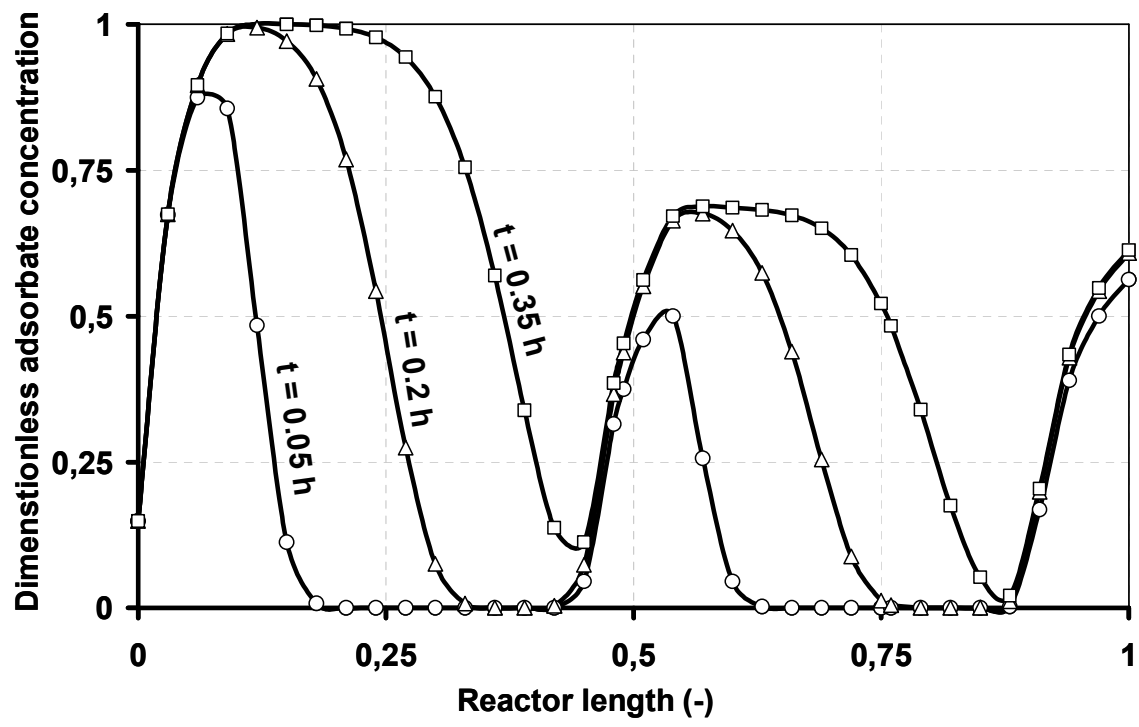


Figure 9: Development of adsorbate concentration fronts in the case of multiple alternate layer catalyst and adsorbent arrangement for 55% minimum conversion for Case-D

## 2.8. Conclusions

In this chapter, an attempt is made to demonstrate the influence of distribution of catalyst and adsorbent pellets on the performance of an adsorptive reactor. Parametric studies were carried out using the kinetics of the Claus process as the benchmark case. A simplified yet adequate model was used to carry out the simulation studies. Using numerical simulations and optimisation studies, it is first demonstrated that one needs to employ an optimal ratio of catalyst to adsorbent in an homogeneously distributed adsorptive reactor. Subsequently, the shortcomings of a homogenous distribution in an adsorptive reactor are identified and it is shown that the optimal solution commonly lies in a non-uniform distribution of catalyst and adsorbent in the reactor. The conditions under which macrostructuring is appropriate are identified as those under which it would lose its efficacy. This chapter thus provides some generic guidelines for the distribution of catalyst and adsorbent functionalities within an adsorptive reactor.

In this study, the concept of optimal distribution is limited to just a simple reversible reaction. Often, in reality, the reaction schemes are neither only a single reaction nor are the process constraints limited to a desired minimum conversion alone. The sorption enhanced steam reforming reaction is a classical example of reaction system with multiple reactions and constraints. Moreover, in contrast to reality, the adsorbent was assumed to be highly selective in this study. Though these idealisation assumptions limit the use of the study's results for quantitative purposes, the qualitative results are indeed valid for real systems and the study clearly highlights the importance of an optimal distribution of catalyst and adsorbent within the reactor.

It is known that the performance of any heterogeneously catalysed reaction system is usually subject to transport resistances and adsorptive reactors are no exception to this rule. One possible approach to reduce transport limitations is to locate the catalyst and adsorbent activities within the same pellet. In the next chapter, the benefits of this micro-integration approach to improve the performance of an adsorptive reactor are analysed.

# **Chapter 3: Spatial distribution of functionalities in an adsorptive reactor at a pellet level**

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## 3.1. Introduction

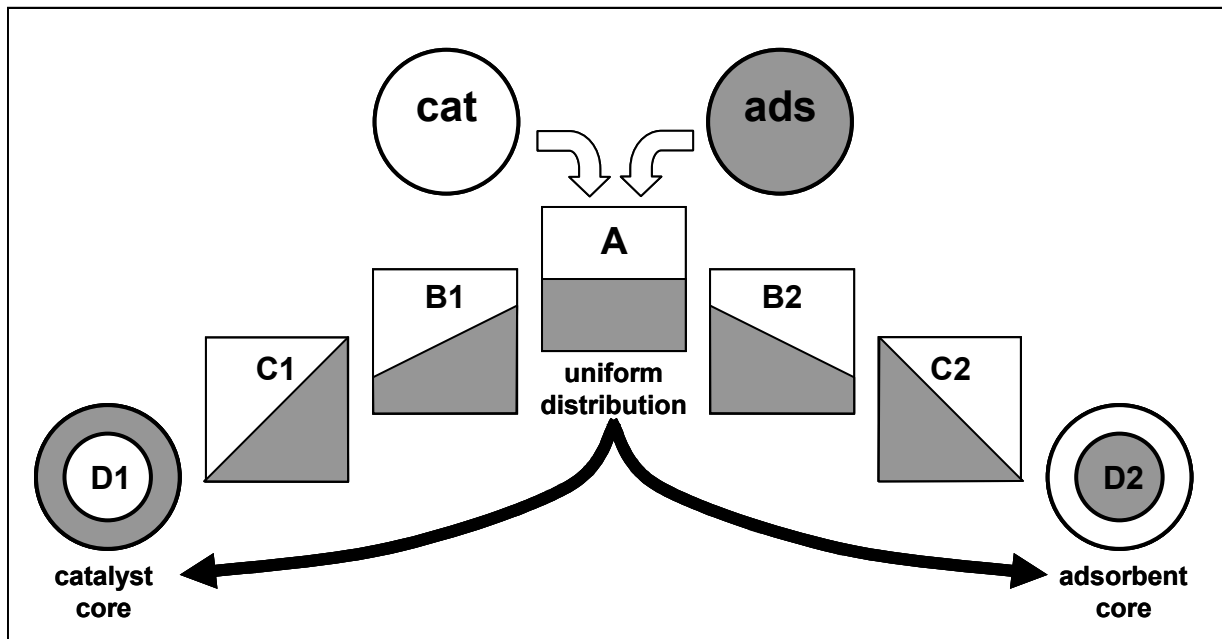
The concept of adsorptive reactors has attracted considerable attention as a hybrid process to enhance reaction selectivity and conversion for heterogeneously catalysed gas phase reactions. An adsorbent is employed as a selective mass source or sink for a particular reaction species (adsorptive) to create favourable concentration profiles within the reactor. Various reaction schemes have been studied experimentally and using numerical simulations to demonstrate the potential of adsorptive reactors. With the recent emergence of hydrogen as an environmental-friendly alternative fuel, considerable effort has been focussed on analysing the possibilities to exploit sorption enhanced processes for hydrogen production [Xiu, Li, Rodrigues, 2003, Hufton, Mayorga, Sircar, 1999]. The Claus process [Elsner, Dittrich, Agar, 2002], total isomerisation process [Aljuhan & Loughlin, 2003], HCN synthesis [Elsner et. al., 2002] and dehydrogenation of methyl cyclohexane [Alpay et. al., 1994] are some of the other reaction schemes which have been studied in the context of adsorptive reactors. Ng et al., [1999] have proposed a direct synthesis of dimethyl ether from synthesis gas using two different catalytic activities in a reactor and recently, this concept has been extended in to a truly multifunctional reactor by the preferential adsorption of water to enhance ether production [Ressler & Agar, 2005].

Studies have been carried out to ascertain strategies for removing process bottlenecks in an adsorptive reactor. One of the various process bottlenecks encountered in an adsorptive reactor is the inefficient utilisation of the adsorbent capacity. In the previous chapter, it has been demonstrated that an expedient distribution of adsorbent (and catalyst) along the adsorptive reactor would improve the performance of adsorptive reactor and the utilisation of the functionalities. Using the Claus process as a test reference case, it has been shown that performance gains in excess of 100% are possible by optimal distribution of functionalities in a reactor as opposed to the uniform axial distribution of functionalities.

It is well-known that, in general, transport limitations are detrimental to the performance of heterogeneous catalysed reactions and adsorptive reactors are no exception to this



rule. In an adsorptive reactor, besides the possible lowering of catalyst effectiveness, transport limitations typically broaden the adsorbate concentration front and thus worsen the performance of adsorptive reactors. One possible to solution to circumvent transport limitations is to combine the functionalities within the same pellet. By integrating the functionalities in this manner, they are brought into closer proximity with one another reducing the unfavourable influence of transport limitations.



**Figure 10: Microstructuring of functionalities: From homogenisation to segregation of functionalities within a pellet**

For the distribution of a single catalytic activity within a pellet, Morbidelli et. al, [1982] have shown that transport limitations are actually not always detrimental to process performance and that by prudent distribution of catalyst activity within a pellet, one can actually exploit the transport limitations to enhance the process performance. This suggests that a more subtle and considered approach to the integration of functionalities at the pellet level is necessary. With only limited knowledge of underlying microstructured functionalities, one can propose a range of possibilities for distributing the functionalities within a pellet optimally, ranging from a uniform distribution to complete segregation of functionalities (Figure 10). In this chapter, we shall analyse the benefits of non-uniformly distributing the functionalities within the pellet space and study the possible improvements achieved by both this pellet-scale integration and microstructuring of adsorptive reactors. For the sake of clarity, the concept of pellet-level distribution is

subsequently referred to as microstructuring. The details on the reaction and kinetic information have already been presented in the previous chapter. In this chapter, the study is extended to identify optimal distribution of functionalities within a pellet.

## 3.2. Modelling of microstructured pellets

In the previous chapter, a two phase heterogenous dispersion model describing the dynamic behaviour of a fixed bed reactor was developed in which the catalyst and adsorbent are present in separate pellets. As the purpose of this chapter is to analyse the performance of microstructured pellets the governing mass balance, the equations presented in the previous chapter need to be modified suitably, but the underlying model assumptions remain the same.

### 3.2.1. Adsorptive reactor model

The microstructured pellets are incorporated in a fixed-bed reactor and a one-dimensional axial dispersion model is used to describe the reactor fluid bulk phase conditions (Equation 13). The third term on the right hand side of Equation 13 accounts for the mass transfer from the fluid bulk phase to the microstructured pellet. It is assumed that only microstructured pellets are present in the reactor.

$$\varepsilon \frac{\partial c_i}{\partial t} = -u \frac{\partial c_i}{\partial x} + D_{ax} \varepsilon \frac{\partial^2 c_i}{\partial x^2} - (1 - \varepsilon) \frac{3}{R_p} k_{film} (c_i - c_p|_{Rp}) \quad \text{- Equation 13}$$

The reactor boundary conditions have been chosen assuming closed vessel behaviour.

$$u \cdot (c_i(x=0, t) - c_{0,i}) = D_{ax} \cdot \frac{\partial c_i(x=0, t)}{\partial x} \quad \text{- Equation 14}$$

$$\frac{\partial c_i(x=L, t)}{\partial x} = 0 \quad \text{- Equation 15}$$

### 3.2.2. Pellet model

Inside the pellets the mass transfer is described using an effective pore diffusion model and the contribution of the adsorption and reaction rates is weighted according to the

volume fractions of the corresponding functionalities in each local pellet volume element resulting in the following expression for the pellet mass balance (Equation 16):

$$\varepsilon_p \frac{\partial c_p}{\partial t} = D_{\text{eff}} \left( \frac{\partial c_p}{\partial r} \frac{2}{r} + \frac{\partial^2 c_p}{\partial r^2} \right) - (1 - \varepsilon_p) (f_{\text{ads}} r_{V,\text{ads}} + f_{\text{cat}} r_{V,\text{cat}}) \quad \text{- Equation 16}$$

The boundary conditions for the pellet mass balance are derived by assuming a linear concentration profiles in the pellet boundary layer (Equation 17) and symmetric profiles within the pellets (Equation 18).

$$k_{\text{film},i} \left( c_i - c_{p,i} \Big|_{r=R_p} \right) = D_{\text{eff},i} \frac{\partial c_{p,i}}{\partial r} \Big|_{r=R_p} \quad \text{Equation 17}$$

$$\frac{\partial c_i}{\partial r} \Big|_{r=0} = 0 \quad \text{- Equation 18}$$

At the outset of each reaction cycle, the reactor contains just an inert component.

$$c_i(x, t = 0) = 0, c_{p,i}(r, t = 0) = 0 \text{ for all } i \neq \text{inert} \quad \text{Equation 19}$$

$$c_i(x, t = 0) = c_{0,\text{inert}}, c_{p,i}(r, t = 0) = c_{0,\text{inert}}, i = \text{inert} \quad \text{Equation 20}$$

The model parameters required were obtained from published data [Elsner et. al., 2002, Elsner, 2004] or calculated using empirical correlations and are summarised in Table 4.

**Table 4: Model parameters and correlations used in this study**

$\varepsilon$	0.4	T	225 °C	Component	Inlet composition
$\varepsilon_p$	0.5	P	1.013 bar	$p_{\text{H}_2\text{S}}$	0.1 bar
$D_i$	$5.55 \times 10^{-5} \text{ m}^2/\text{s}$	$d_p$	2 – 10 mm	$p_{\text{SO}_2}$	0.05 bar
L	1.5 m	D	0.06 m	$p_{\text{N}_2}$	0.85 bar
U	0.15 - 0.30 m/s	$k_{\text{film}}$ & $D_{\text{ax}}$	Wakao, Funazkri [1978]		

### 3.3. Optimisation procedure

The above set of partial differential equations that describe the performance of adsorptive reactors can be solved numerically using equation based solvers. Aspen Custom Modeler<sup>®</sup> was used for carrying out the simulation and optimisation activities.

Any study on the performance of an adsorptive reactor is deemed complete if and only if both the adsorption and desorption steps of an adsorptive reactor are taken into consideration for the performance analysis. Based on the various justifications discussed in the previous chapter, the optimisation study is limited to the adsorption cycle alone.

To compute the optimal catalyst/adsorbent distribution within a microstructured pellet in an adsorptive reactor, the pellet space is subdivided into finite discrete concentric sections and the optimal catalyst fraction in each discrete section is identified. As the optimal microstructure is not unique to a reactor but a function of reactor length, the reactor optimisation space is also divided in to finite sections and studies have been carried out. In this study, the reactor length has been divided up into 13 segments, while the pellet space is subdivided into 5 segments. Though it might be more desirable to obtain a continuous optimal activity distribution profile along the reactor length, the problem is simplified by this discrete approach, which is found to be entirely adequate. Table 5 summarises the optimisation problem and is a pictorial representation of the problem.

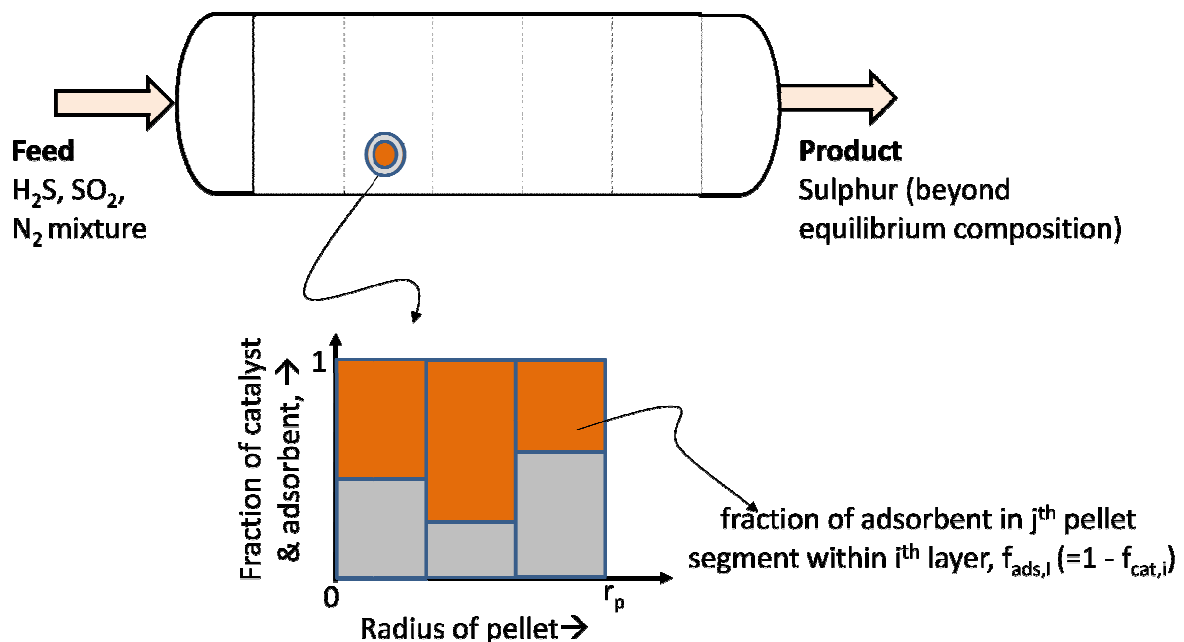
For any given reactor volume, feed flow rate conditions and desired minimum conversion, the process cycle time is a direct measure of the extent of the adsorbent utilisation and thus deemed to be an appropriate objective function for the optimisation process.

As mentioned earlier, dynamic simulation and optimisation studies have been carried out using Aspen Custom Modeler (ACM). The successive quadratic programming optimiser, FEASOPT<sup>®</sup>, which is part of the ACM, has been used to carry out dynamic optimisation. FEASOPT employs a reduced space optimisation method to arrive at the optimal solution. It evaluates the objective function (cycle time) at the current point and moves the decision variables (catalyst fraction values) to take the objective function towards its optimum

value. After solving with the new values of the decision variables, FEASOPT re-evaluates the objective function. In this way, it steps towards the optimum solution. FEASOPT solves the simulation at each step subject to simulation equations, variable bounds and any constraints applied to the optimisation

**Table 5: Description of optimisation problem**

Objective Function	Max. cycle time, $\tau$
Decision variables	Catalyst fraction in any discrete $f(x)_{cat,ij}$  $i = 1, 2, \dots$ no. of pellet segments  $j = 1, 2, \dots$ no of reactor segments
Process constraints	$0 < f_{cat,ij} < 1$  $f_{cat,ij} + f(x)_{ads,ij} = 1$  Conversion $x(t) >$ Desired minimum conversion $x_{min}$



**Figure 11: Scheme for the optimal distribution of functionalities in adsorptive reactor at a reactor level.**

### 3.4. Results and discussion

As adsorptive reactors are operated under unsteady-state conditions, all catalyst and adsorbent pellets are subjected to continuously varying reactant and product concentrations throughout the process cycle and this complicates the task of identifying the optimal microstructure within the pellet. To simplify this task, one needs to discern the different regimes that influence the performance of an adsorptive reactor. The approach to equilibrium ( $\Lambda$ ) is a direct measure of the reaction driving force at any spatial position in the reactor and assists in identification of the different regimes in an adsorptive reactor. It is defined as follows.

$$\Lambda = \frac{\prod_i c_i^{D_i}}{K_{eq}} = \frac{p_{H_2O}^{0.99} k_2}{p_{H_2S}^{0.95} p_{SO_2}^{0.22} k_1} \quad \text{Equation 21}$$

Where

$\Lambda = 1$ , the reaction is at thermodynamic equilibrium

$\Lambda > 1$ , forward reaction occurs

$\Lambda < 1$ , backward reaction occurs

Figure 12 shows the typical variation of  $\Lambda$  along the length of an adsorptive reactor at different cycle times before the process constraint is breached. The figure indicates that the value of  $\Lambda$  is a function of time and reactor space. This graph is typical for a reversible reaction taking place in an adsorptive reactor. Based on this figure, the reactor may be broadly classified into 3 segments. The following discussions focus on the nature of these segments and how they influence the choice of microstructure at any location in an adsorptive reactor. The results of only one of the studies ( $u = 0.3\text{m/s}$ ,  $r_p = 7\text{ mm}$ ) are discussed here for reasons of conciseness. The optimal process cycle time is calculated to be 0.29 h. For the following discussions, normalised concentration profiles are plotted to facilitate comparison. The use of the  $H_2S$  concentration at inlet conditions of the Claus process as the reference value offers one the possibility to compare the relative amounts

of H<sub>2</sub>S and H<sub>2</sub>O present at any point within reactor. The normalised concentration is defined as follows.

$$c_i(r, t) = \frac{c_i(r, t)}{c_{\text{H}_2\text{S, inlet}}} \quad \text{Equation 22}$$

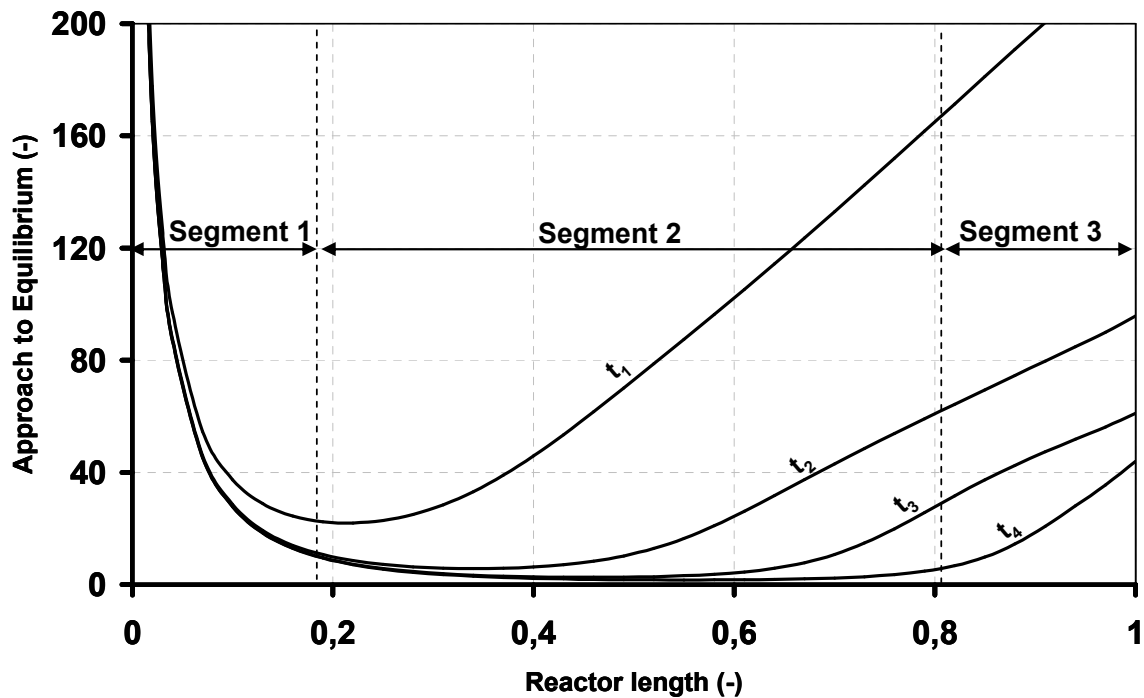


Figure 12: Typical variation of approach to equilibrium  $\Lambda$  along the axial space at different process times for the Claus process ( $r_p = 7\text{ mm}$ ,  $u = 0.25\text{ m/s}$ ). Here  $t_1 < t_2 < t_3 < t_4$

### 3.4.1. Segment – 1

In this segment, the value of  $\Lambda$  is always greater than one and is virtually constant with time. The positive value of  $\Lambda$  indicates that the forward reaction occurs at all times in this segment. It should be noted that of all the reaction occurring in an adsorptive reactor, roughly 80% takes place in the first 20% of the reactor. Figure 13 shows the concentration profile of H<sub>2</sub>S (reactant) and H<sub>2</sub>O (adsorbate) within a microstructured pellet located in this segment at different process times. The reactant concentration profile undergoes little evolution with time and the profiles virtually overlap. In contrast, the adsorbate concentration varies with time indicating the gradual saturation of the adsorbent. However, the product concentration is not significant enough to exert any



influence on the reaction rate and the segment is kinetically controlled. Thus any adsorbent present in this segment plays a secondary, if any, role in its performance.

Based on the work of Morbedelli et. al. [1982], for simple power law kinetics, one can expect that a catalyst shell arrangement would offer the optimal performance. The shaded area in Figure 13 shows the optimal fraction of catalyst in microstructure recommended by the optimiser and the structure closely resembles a catalyst shell arrangement.

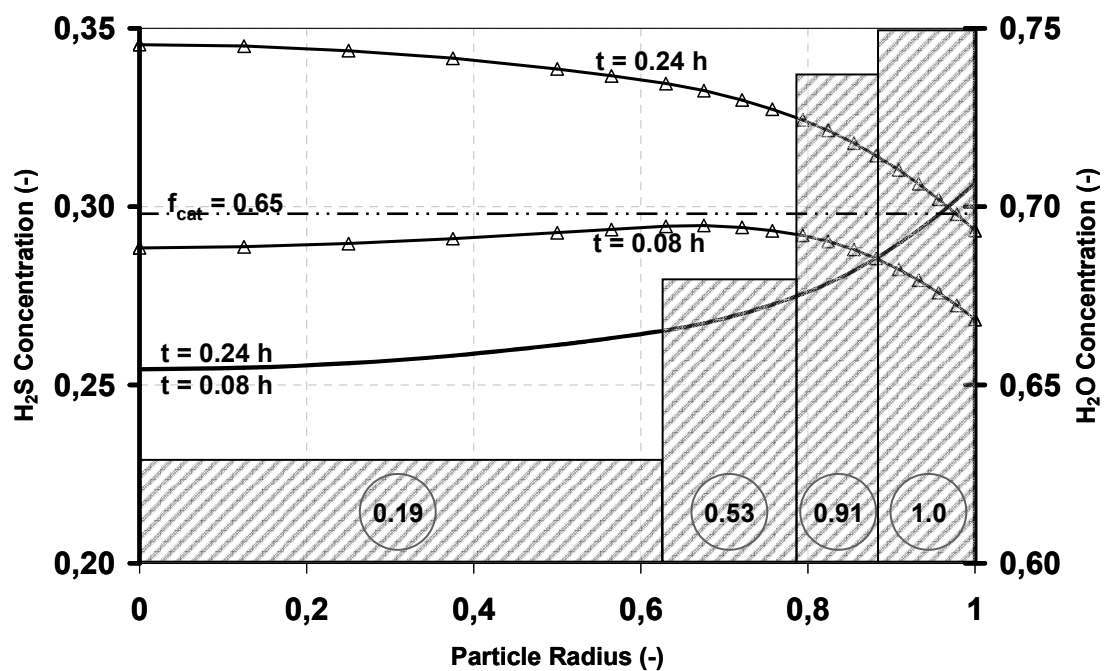


Figure 13: H<sub>2</sub>S and H<sub>2</sub>O concentration profile within a microstructured pellet located 135 mm from reactor entrance. The shaded areas and the circled numbers indicate the optimal catalyst fraction at any location within pellet.

- △— Concentration of H<sub>2</sub>O
- Concentration of H<sub>2</sub>S
- Optimal uniform catalyst fraction

### 3.4.2. Segment – 2

Unlike the previous segment, this segment is characterised by a dynamic variation of  $\Lambda$  with space and time (Figure 12). At any point, while the adsorbent is unsaturated,  $\Lambda$  is greater than one. Upon adsorbent saturation, however, the value of  $\Lambda$  becomes one and

this indicates that equilibrium has been achieved. Thus though the segment is initially kinetically controlled, the sorption regime gradually sets in. Figure 14 illustrates the concentration profile of H<sub>2</sub>S (reactant) and H<sub>2</sub>O (adsorptive) within a microstructured pellet located in this segment at different process times.

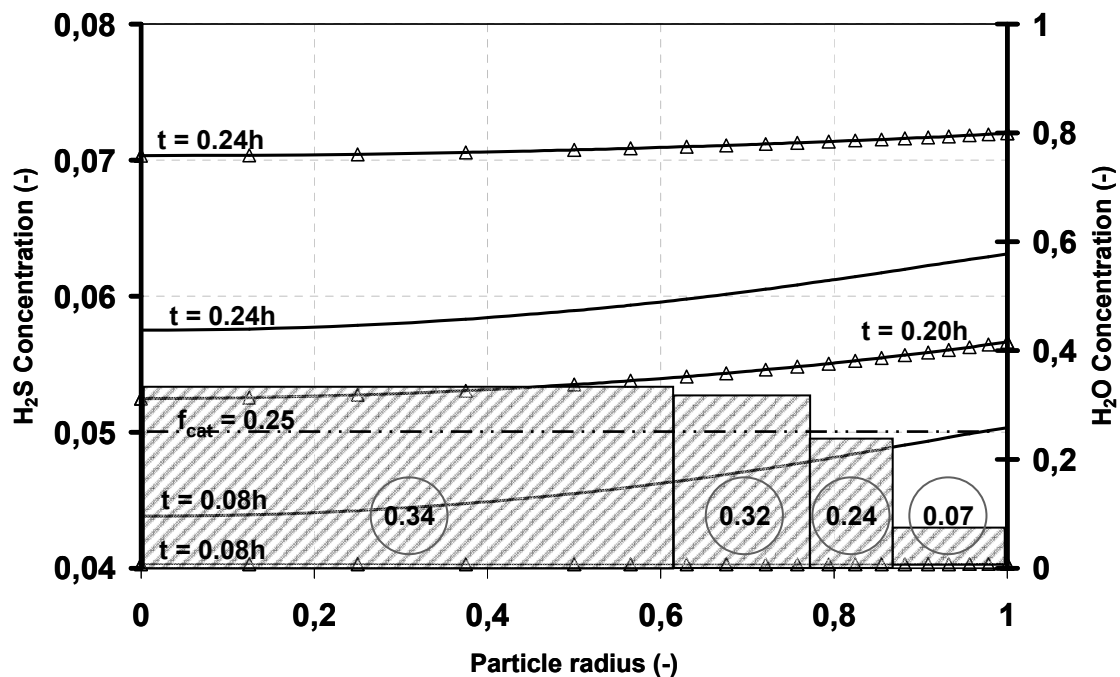


Figure 14: H<sub>2</sub>S and H<sub>2</sub>O concentration profile and optimal microstructure within a microstructured particle located at 675mm from reactor entrance. Refer Figure 13 for legend.

As the predominant portion of all reaction taking place in an adsorptive reactor is limited to segment 1, the concentration of reactant is conspicuously low in the second segment. This, compounded with higher product concentrations, leads one to expect that the rate of reaction will be slower than in segment 1. Thus, the adsorption of product is vital for the forward reaction to occur in this regime. The shaded area in Figure 14 shows the optimal microstructure of the pellet recommended by the optimiser. The low reaction rates place lower demands on the need for a catalyst shell arrangement for the effective utilisation of the catalyst activity. For this reason, the functionality distribution within pellet tends to be rather uniform. The high adsorbent fraction in the pellet shell is attributed to the importance of adsorptive removal to sustain the forward reaction.

### 3.4.3. Segment – 3

The behaviour of this segment is basically similar to segment 2 and may be considered as its extension. What distinguishes these two segments is that, unlike segment 2, the adsorbent in section 3 remains unsaturated even up to the breach of the process constraint. The adsorptive concentration front does not really breakthrough into this segment before the breach of process constraint. Thus, any adsorbate present in this segment primarily originates within it and hence the adsorbate concentration is not especially significant here. This means that the segment is kinetically controlled throughout the process cycle. Figure 15 shows the concentration profile of H<sub>2</sub>S (reactant) and H<sub>2</sub>O (adsorbate) within a microstructured pellet located within this segment at different process times and the corresponding optimal microstructure. As the segment is kinetically controlled, the optimal microstructure resembles a catalyst shell similar to that observed in segment 1.

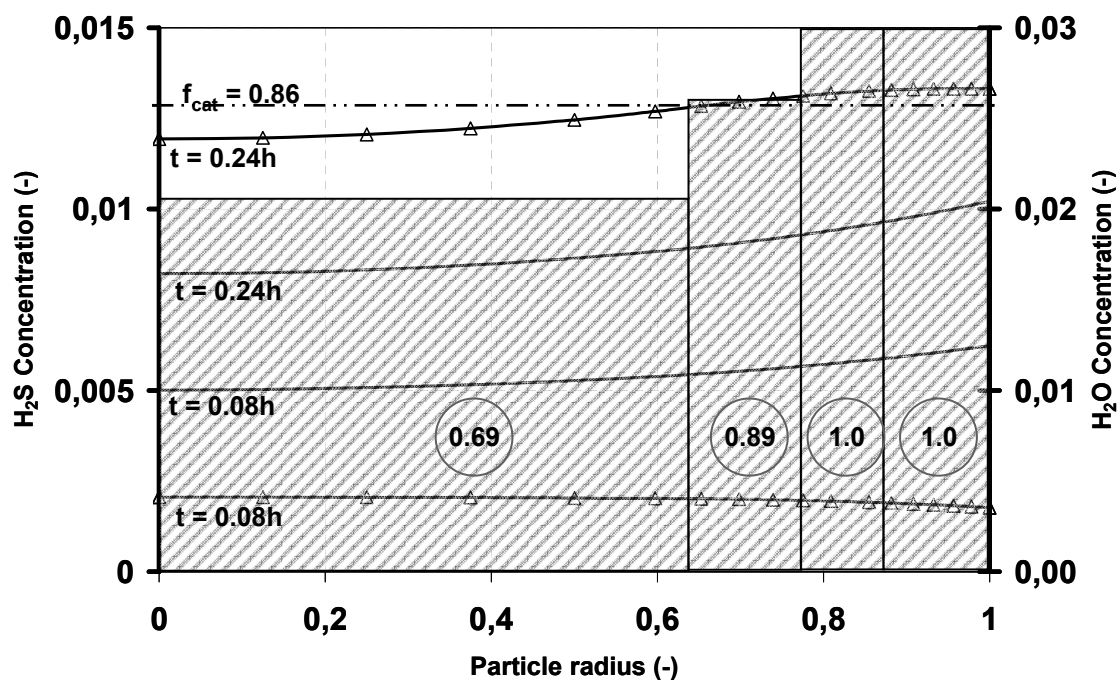


Figure 15: H<sub>2</sub>S and H<sub>2</sub>O concentration profile and optimal microstructure within a microstructured pellet located at 1335mm from reactor entrance. Refer Figure 13 for legend

It may be argued that the existence of segment 3 is a characteristic of the Claus reaction, by virtue of its very rigorous process termination conditions (Sulphur recovery

efficiency > 99.5%). However, it should be noted that the existence of segment 3 is not uncommon in adsorptive reactors and a similar zone has been suggested for steam reforming reaction in adsorptive reactors [Xiu et. al., 2003]

### 3.5. Relevance of structuring

From the previous discussion, it is obvious that the choice of pellet microstructure is unique to the regime that is governing the pellet behaviour. In order to study the importance of the non-uniform distribution of functionalities within the pellet, an additional optimisation run for the above test case was carried out with only one pellet layer (i.e. a uniform pellet distribution case), while the same number of axial discrete sections was retained. The broken lines in Figure 13 and Figure 14 show the optimal uniform catalyst fraction recommended by the optimiser. It is found that though the functionality distribution profile is different, the performance of the uniform and non-uniform microstructures is comparable (less than 3% difference in cycle time). This suggests that a simple pellet level integration of functionalities can perform as well as any optimal microstructure and the marginal difference in performance is attributable to the following causes:

- in general, the combined width of segment 1 and 3 is less than 20% of the total reactor length. Thus, even though a uniform distribution is far from a truly optimal microstructure, the relatively short span of these segments limits their influence on the overall performance of the reactor. In addition, though a kinetically controlled regime exists in segment 3, the reaction rate itself is too low to exert a significant influence on the overall performance of the reactor.
- the optimal microstructure in segment 2 is not far from a uniform distribution of functionalities within a pellet anyway. Furthermore, segment 2 occupies a major portion of the total bed length and thus exerts a significant influence on the overall reactor performance.

### 3.6. Realities of microstructuring

All of the above observations indicate the limitations on the application of microstructuring to the Claus process. But can microstructuring of adsorptive reactors ever be a successful concept for other adsorptive reaction systems? The answer to this question may be found by comparing the typical diffusion time constants in a pellet to the process cycle times. The diffusion time is defined as the time needed by a molecule at the pellet surface to diffuse into the pellet (of the order of  $\frac{R_p^2}{D_{eff}}$ ). Typical diffusion times for gas phase systems are in the range of 0.01 to 2 s.

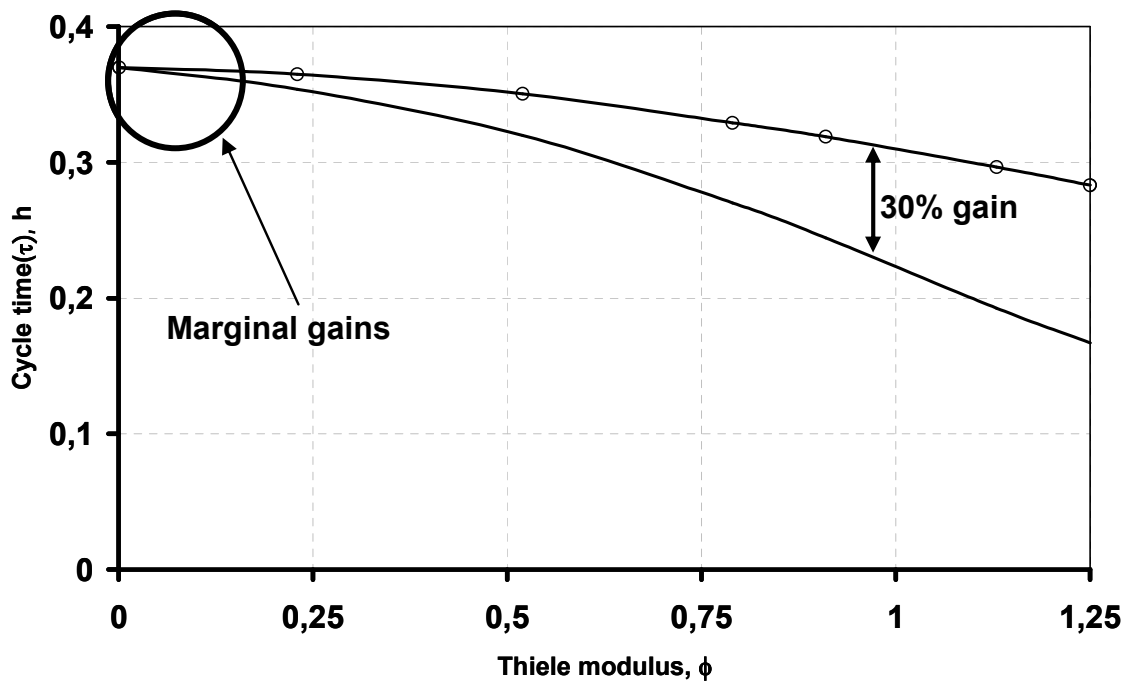


Figure 16: Influence of transport resistance on process cycle time in Claus process: Comparison of performance by conventional adsorptive reactor to micro-integrated adsorptive reactor

- Micro-integrated particles
- Reactor with mixture of catalyst and adsorbent particles

In comparison to the relatively small diffusion times, the process cycle times are significantly higher (of the order of minutes to hours) and thus provide ample time for the diffusion to take place leaving the system free of any significant diffusion limitations in the sorption regime. This is also the reason for satisfactory performance of Glueckauf's

linear driving force approximation in predicting adsorption processes. If the diffusion time constants and the process cycle time were to be comparable, then microstructuring would have had a significant impact on the performance of the adsorptive reactor.

### **3.7. Conclusions**

In this work, an attempt has been made to understand the influence of distribution of catalyst and adsorbent functionalities at the pellet level on the performance of an adsorptive reactor using the Claus process as a reference case. The study reveals the existence of distinct regimes that govern the performance of an adsorptive reactor. The regimes determine the choice of the optimal microstructure at any location within the reactor. Though a non-uniform distribution of functionalities is found to be optimal, the performance of an optimal uniform distribution is nevertheless comparable. Thus, the utility of functionality microstructuring may be limited to the micro-integration of functionalities at the pellet level. Micro-integration of functionalities is found to be a useful tool to circumvent transport limitations in an adsorptive reactor. Though it is not explicitly described here, the optimal distribution of functionalities in an adsorptive reactor also implicitly involves a non-uniform distribution of functionalities at the reactor level.



# **Chapter 4: Thermal integration of functionalities at a pellet level – A case study for an oxidative dehydrogenation process**

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## 4.1. Introduction

Many industrially relevant chemical reactions are plagued by thermodynamic equilibrium limitations and selectivity problems, and it is not uncommon that mass and energy transport limitations aggravate the situation. The synthesis of ethylene oxide is a classical example of a process that may underperform, due to limitations in heat dissipation. Conventionally, ethylene oxide is manufactured by the oxidation of ethylene in a multi-tubular packed bed reactor. The ethylene oxide formation reaction and the competing combustion reaction are highly exothermic, resulting in the formation of thermal hotspots, and hence a lower selectivity. Krishna and Sie [1994] recommend a ramped catalyst distribution at the reactor entrance to control the hotspot formation. This ramped catalyst arrangement lowers the hotspot temperature and results in an improved selectivity towards ethylene oxide. Essentially, this solution involves a tacit reduction in reaction rate at reactor entrance as a means to control the temperature profile within reactor, harmonising the exponential rate of heat liberation with the linear rate of heat removal. Thus, a better selectivity is achieved at the expense of space time yield of reactor and this highlights the need for a more efficient heat dissipation system. Microreactors offer a suitable alternative to overcome the bottlenecks of multi-tubular reactors and recently, Kestenbaum et. al., [2002] have demonstrated that microreactors offer minimal temperature gradients ( $\Delta T < 1\text{K}$ ) for ethylene oxidation even in the absence of diluents, this being attributed to their superior heat dissipation performance.

In contrast to using conventional recuperative heat dissipation or supply systems, several innovative heat source/sinks have been studied in an attempt to improve the overall performance of reactors. Recently, Richarth et. al., [2005] have employed adsorbents within reactor as a regenerative heat sink to control and manipulate the temperature profile during an exothermic reaction. As the adsorbent capacity is limited, there is a need for a periodic loading of the adsorbent. Maruoka et. al., [2004] have studied the possibility of developing a new heat recovery system for hot waste gases from steel-making industry. Here, the heat from the hot gases is stored in phase change materials

(PCMs) and is then supplied to an endothermic methane-steam reforming process in a regenerative fashion.

The concept of coupling a reactive heat source/sink also have been extensively studied and is indeed practiced in industry. Fluidised catalytic cracking is an important industrial petrochemical process, where a reactive heat source is employed, and in this multifunctional reactor [Dauzenberg, 2001], the silica-alumina catalyst pellets are used as energy carriers between the endothermic catalytic cracking section and the exothermic regenerator section. Steam reforming used in hydrogen generation and syngas production is another thermally intensive industrial process, which has attracted considerable attention from multifunctional reactor researchers to find suitable alternatives to improve process economics. Stitt [2004] reviewed the various multifunctional concepts explored in the literature to improve the steam reforming process, including the possibility of combining the endothermic steam reforming reaction with exothermic oxidation/combustion reactions. Different approaches have been adopted, each varying in the degree of complexity and the intimacy of reactive coupling:

- autothermal reforming reactors (ATR) where the methane oxidation and reforming reaction are combined, if somewhat segregated, within the same reactor
- fluidised bed reactors, where the fluidised pellets allow a dynamic regenerative heat exchange between the different zones of the reactor
- wall reactors, where the oxidation and reforming catalyst are supported on either side of a dividing wall. Heat transfer occurs across the wall direct from the oxidation to the reforming catalyst.
- asymmetric operation of a fixed-bed, which is a combination of the reactive coupling and reverse flow concepts, with the oxidation reaction serving to heat the fixed-bed, which is subsequently cooled as it catalyses the endothermic reforming reaction.

The concept of reactive heat coupling has not been limited to steam reforming reactions alone. Kolios and Eigenberger [1999] studied the coupling of a dehydrogenation of ethylbenzene to styrene with the combustion of the hydrogen produced in a periodic

reverse-flow reactor. This concept had also been suggested previously by Levenspiel for the RE-GAS process for coal gasification [Kolios et. al., 2000].

In addition to the above examples of reactor scale integration of multiple functionalities, one can also harness the catalyst pellet space by combining multiple functionalities within pellet to intensify chemical processes. This idea of multifunctionalisation of pellet space has been extensively studied in the past. In the case of dimethyl amine synthesis, Foley [1994] has employed carbon molecular sieves to manipulate the diffusion of certain specific reaction species at a pellet scale to improve the selectivity. Hünemann et. al., [2005] have experimentally studied the possibility of co-immobilising multiple enzymes within the same pellet. The possibilities of combining catalyst and adsorbent at a pellet scale as a method to circumvent transport limitations in an adsorptive reactor are discussed earlier in this thesis [Lawrence et. al., 2005]. This multifunctional catalyst concept could also be extended to carry out reactive heat coupling at a pellet level and here we shall study the potential for combining multiple functionalities at a pellet scale as a means to effectively transfer heat within a chemical reactor. It should be noted here that the motivation for combining independent catalyst activities within a single pellet is to couple the functionalities in terms of mass and heat transport mechanisms over microscopic dimensions and this principally differentiates such multifunctional catalyst from bi-metallic catalysts and their like [Frakas 2001]. On this basis, the pellet-scale reactive heat coupled multifunctional catalysts can be grouped under Dautzenberg's Type B method of multifunctionalisation.

The concept of pellet scale reactive heat coupling is not completely new. Studies on oxidative dehydrogenation and oxidative steam reforming reactions have already been conducted to carry out reactions under thermoneutral conditions. In these studies, the choice of catalyst is such that a single catalyst activity catalyses both the exothermic and endothermic reaction. A key drawback of such a scheme is that one has limited options to regulate the participating reactions independently and the process selectivity relies primarily on the choice of catalyst. In the case of the proposed multifunctional catalyst, the presence of two distinct catalytic activities offers an additional degree of freedom in the hands of the process designer to optimise process performance.

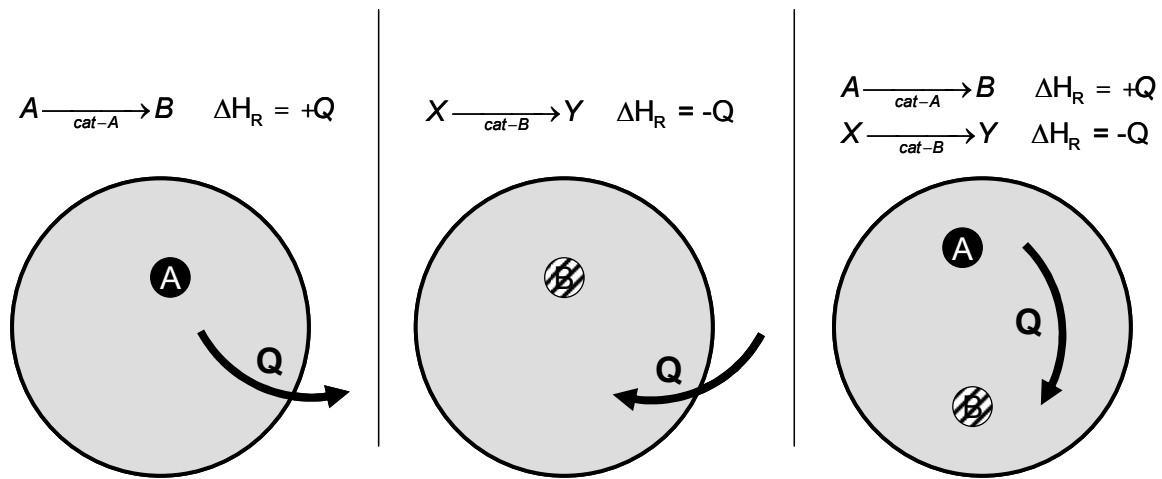


Figure 17: Concept of reaction heat coupling in a multifunctional catalyst pellet

#### 4.1.1. Micro-scale heat integration concept

Heterogeneous catalytic reactions are subject to mass and energy transport phenomena in the catalyst pellet. Though these transport processes often limit the catalyst performance, at times they can be prudently manipulated to improve catalyst performance [e.g. Morbedelli et. al., 1982]. In the case of heat transport, the resistance predominately lies in the boundary layer film surrounding the catalyst pellet (indicated by low Biot numbers) and literature review suggests that temperature drop across the film could be significant (e.g. Kehoe and Butt, 1972). Any drop in temperature across the film can significantly alter the catalyst effectiveness and in addition, may cause undesirable multiple steady-states [Sie and Krishna, 1998] in the case of exothermic reactions. For an endothermic reaction, the energy transport limitation results in a lower catalyst effectiveness and one strategy to overcome the limitation is to introduce the reactive heat source within the pellet itself. By thermal coupling of an exothermic and endothermic reaction within the same pellet, one can enhance the endothermic reaction utilising the energy supplied by its exothermic counterpart.

Gray and Ball [1999] have studied a novel reactor scheme (Endex reactors) for thermal control of potentially runaway reactions. The Endex reactor is a composite of individual CSTRs, each of which houses either an exothermic or endothermic reaction mixture. It

has been shown that when heat is exchanged freely between the two CSTRs (i.e. the temperature of the two CSTRs are the same) and under perfectly matched reaction conditions, the upper steady-state (in multiple steady-state) of the exothermic reaction occurs at a relatively lower and manageable temperature. In addition, it has been shown to be feasible to operate the reactor at this high conversion steady-state condition. The close proximity of the reactive heat source and sink in the case of pellet-scale reactive heat coupling allows a rapid heat exchange between heat source and sink and, in a way, this may be considered as similar to the conditions in the Endex reactor concept and hence one can expect to operate to such pellets safely at the high conversion steady-state conditions for the exothermic reaction. Thus pellet scale reactive heat coupling can improve the catalyst effectiveness of the endothermic reaction, as well as allowing the exothermic reaction be operated at the more productive upper steady-state conditions.

The focus of the present study is on combining reactions that are catalysed by two distinct catalysts, the ratio of the two catalysts within the pellet offers an additional degree of freedom to control the reactions and thus influence the catalyst performance. In this work, we intend to demonstrate the concept of micro-integration of an exothermic and endothermic reaction within a single catalyst pellet and illustrate the conditions under which such coupling is beneficial.

## 4.2. Test reaction scheme

Styrene is a versatile monomer used extensively in the manufacture of plastics, including polystyrene and various other copolymers. It is primarily manufactured by the catalytic dehydrogenation of ethylbenzene. The reaction is highly endothermic and reversible in nature. As a consequence, most commercial styrene processes operate under low conversion per pass, high steam to hydrocarbon ratio and subatmospheric pressure conditions. Several research initiatives have been embarked upon to improve the process economics. Membrane reactors, oxidative dehydrogenation of ethylbenzene and ethylbenzene dehydrogenation using  $\text{CO}_2$  as soft oxidant are some of the alternative approaches studied to overcome the drawbacks of the conventional process. In addition to these, Lummus/UOP has recently commercialised a process (SMART process) where a reactive heat source is incorporated within the reactor to supply heat for the dehydrogenation reaction. The reactors are loaded with dehydrogenation and oxidation catalysts in adjacent beds and in the oxidation section, hydrogen is oxidised to supply the heat of reaction for the dehydrogenation reaction. In addition to supplying the heat of reaction, as hydrogen is consumed in the oxidation step, the dehydrogenation reaction equilibrium is shifted towards the products through reduction in hydrogen partial pressure (Table 6). Though the commercial viability of the process attests to the success of concept, any advocate of pellet-scale heat coupling would contend that the spatial segregation of catalysts within reactor might impede the process performance and would propose a pellet-scale heat coupling to improve process performance. In this study, the SMART process is used as a test reaction scheme to analyse the benefits of coupling an exothermic and endothermic reaction at a pellet-scale. In addition to investigating the test case, the study is extended to a generic reaction scheme in order to identify the conditions under which pellet-scale thermal coupling is advantageous.

Table 6: Dehydrogenation reaction scheme for styrene and by-products formation [Ahari et. al., 2004]. Hydrogen oxidation kinetics is Hoiberg et. al., [1971]

<b>Dehydrogenation reaction scheme</b>	
$C_6H_5CH_2CH_3 \leftrightarrow C_6H_5CHCH_2 + H_2$	Equation 23
$r_1 = k_1 \left( p_{EB} - \frac{p_{sty} p_{H_2}}{K_{EB}} \right)$	
$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4$	Equation 24
$r_2 = k_2 p_{EB}$	
$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$	Equation 25
$r_3 = k_3 p_{EB} p_{H_2}$	
$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$	Equation 26
$r_4 = k_4 p_{C_2H_4} p_{H_2O}$	
$CH_4 + H_2O \rightarrow CO + 3H_2$	Equation 27
$r_5 = k_5 p_{CH_4} p_{H_2O}$	
$CO + H_2O \rightarrow CO_2 + H_2$	Equation 28
$r_6 = k_6 \left( \frac{P_T}{T^3} \right) p_{CO} p_{H_2O}$	
<b>Oxidation reaction</b>	
$2H_2 + O_2 \rightarrow 2H_2O$	Equation 29
$r_7 = k_7 p_{O_2}^{0.8}$	



Recently, Ahari et. al., [2004] used industrial plant data to estimate the kinetic parameters for a proposed set of reactions used to describe the styrene process. A pseudo-homogenous model was proposed and the kinetic parameters were used as fitting parameters to describe the SMART process. Table 6 shows the proposed reaction scheme. The oxidation catalyst was assumed to be highly selective for hydrogen oxidation and the kinetics proposed by Hoiberg et. al., [1971] were employed. For the three reactor-in-series SMART process, the pseudo-homogenous model has a good predictive capability for the first reactor, though the accuracy diminishes for the second and third reactors. Though the model has predictive capabilities, the kinetic information is extrinsic in nature and needs correction for the mass and heat transport processes occurring within the pellet. The kinetics of Ahari et. al., [2004] have been corrected for transport limitations within reactor and the intrinsic microkinetics thus derived have been therefore used in this study.

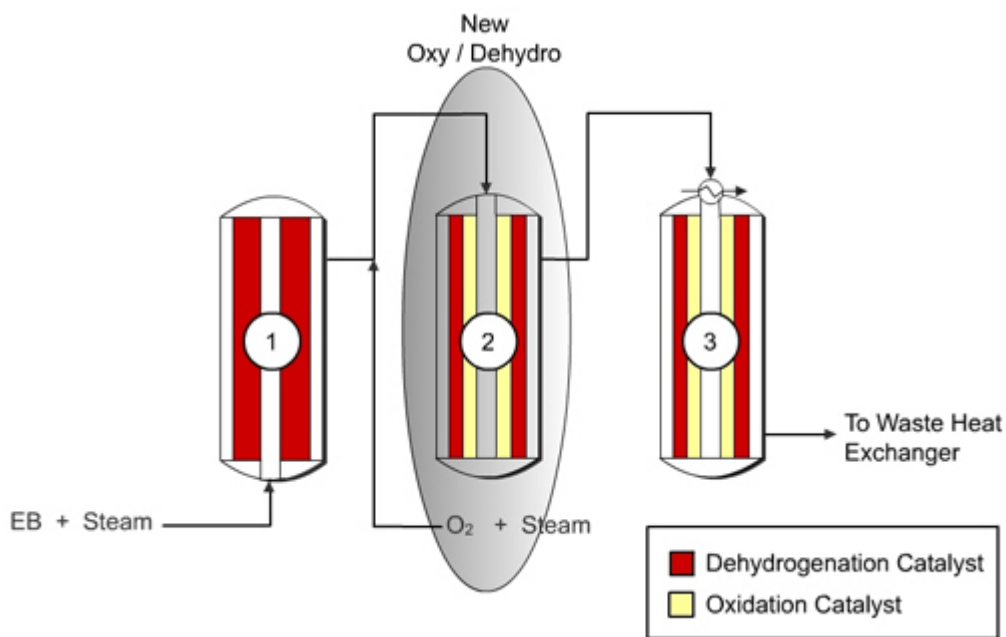


Figure 18: Styrene manufacture by SMART process

Table 7: Dimensions of the reactors in SMART process (Ahari et. al., 2004]

Reactor number	Oxidation bed diameter (m)		Dehydrogenation bed diameter (m)		Height (m)
	Inner (ID1)	Outer (OD1)	Inner (ID2)	Outer (OD2)	
1	-	-	0.99	2.108	6.08
2	0.91	1.35	1.35	2.47	6.353
3	1.150	1.52	1.52	2.57	6.393

Table 8: Comparison of model predictions against plant data

Model	Ethylbenzene (kmol/h)	Styrene (kmol/h)	Benzene (kmol/h)	Toluene (kmol/h)	Temperature, K	
					Oxidation bed (maximum)	Reactor exit
<b>Reactor I</b>						
Industrial data	95.68	54.33	0.678	1.358		544.4
Pseudo-homogenous	94.49	55.03	0.975	1.863		554.7
Heterogeneous	95.99	54.33	0.678	1.358		555.2
<b>Reactor II</b>						
Industrial data	55.14	91.67	1.89	3.34	624.93	574.83
Pseudo-homogenous	57.73	90.18	2.04	2.44	636.37	593.10
Heterogeneous	58.45	90.76	1.39	1.76	631.57	587.67
<b>Reactor III</b>						
Industrial data	28.14	91.67	1.89	3.34	624.93	574.83
Pseudo-homogenous	34.92	90.18	2.04	2.44	636.37	593.10
Heterogeneous	43.15	105.69	1.71	1.81	613.65	608.94

## 4.3. Modelling of heat coupled pellets

A heterogeneous two-phase, adiabatic, radial flow reactor model describing the behaviour of a fixed-bed reactor with separate catalyst phase has been developed. In addition to a model where the two catalyst functionalities are coupled within the same pellet, a second model is developed where the two catalyst functionalities are present in separate pellets. The intrinsic parameters are estimated using the second model and this model also acts as a benchmark case to compare the performance of the pellet-scale heat-integrated situation.

The models are based on the following simplifying assumptions:

- Ideal plug flow conditions in the radial flow direction. Radial flow occurs in the centrifugal direction and no axial flow occurs.
- Transport occurs in the porous catalyst by diffusion alone.
- All heat transport is localised in the film around the pellet and pellet itself is assumed to be isothermal.
- the physical structure of the pellet can be idealised as porous spheres with a uniform pore structure
- the gas phase behaviour obeys the ideal gas law
- the catalyst activity within a pellet is uniformly distributed

### 4.3.1. Pellet model

Inside the pellets, the mass transfer is described using an effective pore diffusion model and the following expression gives the mass balance for coupled catalyst pellet.

Heat coupled catalyst pellet:

$$D_{\text{eff},i} \left( \frac{d^2 c_{p,i}}{dr^2} + \frac{2}{r} \frac{dc_{p,i}}{dr} \right) = - \sum_{j=1}^6 \nu_{ij} r_j f_{De} + \nu_{i,7} r_7 f_{oxy} \quad \text{Equation 30}$$

For the benchmark system, the dehydrogenation and oxidation catalyst are present in separate pellets and separate mass balance equations are written for these pellets as given below:

Oxidation catalyst pellet:

$$D_{\text{eff},i} \left( \frac{d^2 c_{p,i}}{dr^2} + \frac{2}{r} \frac{dc_{p,i}}{dr} \right) = -\nu_{i,7} r_7 \quad \text{Equation 31}$$

Dehydrogenation catalyst pellet:

$$D_{\text{eff},i} \left( \frac{d^2 c_{p,i}}{dr^2} + \frac{2}{r} \frac{dc_{p,i}}{dr} \right) = -\sum_{j=1}^6 \nu_{i,j} r_j \quad \text{Equation 32}$$

The boundary conditions for the pellet are derived by assuming a linear concentration profiles in the pellet boundary layer (Equation 33) and symmetric profiles at pellet centre (Equation 34).

$$k_{\text{film}} (c_i - c_{p,i} \Big|_{r=R_p}) = D_{\text{eff},i} \frac{dc_{p,i}}{dr} \Big|_{r=R_p} \quad \text{Equation 33}$$

$$\frac{dc_i}{dr} \Big|_{r=0} = 0 \quad \text{Equation 34}$$

As the heat Biot number ( $Bi_h$ ) indicates that resistance to heat transfer primarily resides in the film surrounding catalyst pellet, the temperature within pellet is assumed to be uniform. The heat balance for the pellet phase in the case of coupled catalyst case and benchmark case is given by Equation 35 and Equation 36.

Oxidation/ Dehydrogenation catalyst pellet:

$$\frac{6}{d_p} h_{\text{film}} (T_p - T) = \sum r_{\text{avg},j} (-\Delta H_j) \quad \text{Equation 35}$$

Heat coupled catalyst pellet:

$$\frac{6}{d_p} h_{\text{film}} (T_p - T) = \sum_{j=1}^6 r_{\text{avg},j} (-\Delta H_j) f_{De} + r_{\text{avg},7} (-\Delta H_7) f_{oxy} \quad \text{Equation 36}$$

### 4.3.2. Reactor model

The pellet models are incorporated in a fixed-bed reactor and a one-dimensional plug flow reactor model is used to describe the reactor fluid bulk phase for the two models. The term on the right hand side of Equation 37 accounts for the mass transfer from the bulk phase to the catalyst pellets.

$$-\frac{dF_i}{dz} = (1-\varepsilon_b)A_z \frac{6}{d_p} k_{\text{film}} (c_i - c_{p,i}) \quad \text{Equation 37}$$

In the case of benchmark system, the reactor mass balance is given by the following expression:

$$-\frac{dF_i}{dz} = (1-\varepsilon_b)A_z \frac{6}{d_p} k_{\text{film}} (c_i - c_{p,i}) f_{oxy} + (1-\varepsilon_b)A_z \frac{6}{d_p} k_{\text{film}} (c_i - c_{p,i}) f_{De} \quad \text{Equation 38}$$

The reactor energy balance for the pellet scale heat integrated pellets and the benchmark system are given in Equation 39 and Equation 40 respectively.

$$\left(\sum F_i C_{p,i}\right) \frac{dT}{dz} = A_z (1-\varepsilon_b) \frac{6}{d_p} h_{\text{film}} (T_p - T) \quad \text{Equation 39}$$

$$\left(\sum F_i C_{p,i}\right) \frac{dT}{dz} = A_z (1-\varepsilon_b) \frac{6}{d_p} h_{\text{film}} (T_p - T) f_{oxy} + A_z (1-\varepsilon_b) \frac{6}{d_p} h_{\text{film}} (T_p - T) f_{De} \quad \text{Equation 40}$$

The reactor boundary conditions have been chosen by assuming closed vessel behaviour. The pressure drop across the fixed bed is estimated using the Ergun equation.

In addition to the above models, a simple short-cut pseudo-homogenous model was also developed.

## 4.4. Estimation of intrinsic kinetics & model capabilities

As the focus of this study is to analyse the benefits of microscale coupling of a reactive heat source and sink within a pellet, one needs to ensure that the kinetics are intrinsic and not falsified by transport limitations. As the styrene kinetics available in literature for SMART process [Ahari et al, 2004] are extrinsic in nature, the required intrinsic kinetics were extracted using additional literature sources.

Using Ahari's extrinsic kinetics in the rigorous heterogeneous model suggests that the effectiveness factor of dehydrogenation catalyst is typically of the order 0.90 under industrial conditions. Further, a low Weisz-Prater number (at reactor entrance conditions) suggests that the transport limitations are not very significant. Under these conditions, Elnashaie and Elshishini [1993] suggest an iterative procedure to extract intrinsic kinetics from "falsified" kinetic information. Employing this procedure, frequency factors for the participating reactions are iteratively modified by suitable multiplying factors until the model prediction matches the industrial data, while the activation energies of these reactions are held constant. Though Elnashaie and Elshishini [1993] suggest that the components resulting from a single reaction i.e., styrene, toluene, benzene and carbon dioxide be multiplied by factors arising from the ratio of industrial molar flow rates to that estimated by the heterogeneous model, the lack of industrial data for carbon dioxide has restricted us to applying this concept to the remaining three components alone. Moreover, as the influence of reactions involving steam (Equation 26, Equation 27 and Equation 28) are less significant on the overall process, their frequency factors were maintained at values proposed by Ahari et. al., [2004] On this basis, the intrinsic kinetic parameters were re-estimated from the apparent kinetics using an iterative procedure. 35 iterations were required for convergence and shows the microkinetics thus obtained for the styrene process.

**Table 9: Apparent frequency factors and new intrinsic frequency factors for styrene process reactions**

Reaction	Frequency factor		Activation energy
	Apparent	Intrinsic	
1	0.02	0.02306	$8.071 \times 10^4$
2	19.4	16.213	$25 \times 10^4$
3	0.3	0.7368	$8,73 \times 10^4$
4	0.12	0.12	$1,03996 \times 10^4$
5	-3.21	-3.21	$6,5723 \times 10^4$
6	21.21	21.21	$7,6382 \times 10^4$

Table 9 shows the comparison of results predicted by pseudo-homogenous model and rigorous heterogeneous model against the industrial data for day 1 (see Ahari et al., 2004). From the data, it is obvious that predictions of the rigorous heterogeneous model are more realistic in comparison to the pseudo-homogenous model for reactors I and II, sthough the model severly underestimates the conversion in the case of reactor III. The decrease in accuracy may be attributed to the lack of actual reactor entrance pressure and temperature values and a fortuitous choice of the oxidation kinetics.



## 4.5. Pellet scale heat integration

Considering the present reactor configurations of the SMART process, the concept of pellet-scale heat integration could only be applied to reactors II and III. As the purpose of the study is to understand the influence of pellet-scale integration, rather than to improve the performance of SMART process, we have restricted our studies to reactor II alone.

Prior to applying pellet-scale heat coupling, one needs to be aware of the sections within reactor II in which the concept could be applied to advantage. The approach to equilibrium is a useful tool to identify the extent of driving force available for a reversible reaction to occur. The approach to equilibrium is defined as follows:

$$\Lambda = \frac{P_{EB}}{P_{Sty}P_{H_2}} K_{EB} \quad \text{Equation 41}$$

For  $\Lambda = 1$ , the reaction is at thermodynamic equilibrium

$\Lambda > 1$ , forward reaction occurs

$\Lambda < 1$ , backward reaction occurs

shows the variation of approach to equilibrium for the ethylbenzene dehydrogenation reaction. The reaction mixture entering the reactor II is fairly close to equilibrium. In the oxidation bed, additional driving force for the dehydrogenation reaction is created by reduction in hydrogen partial pressure as a result of hydrogen oxidation. Moreover, as the dehydrogenation reaction is endothermic, the increase in bed temperature due to oxidation also provides an additional driving force. The reverse of the above process then takes place in the dehydrogenation bed resulting in the lowering of the reaction driving force. Based on the above arguments, it is to be expected that any dehydrogenation catalyst present in the reactor entrance may be ineffective.

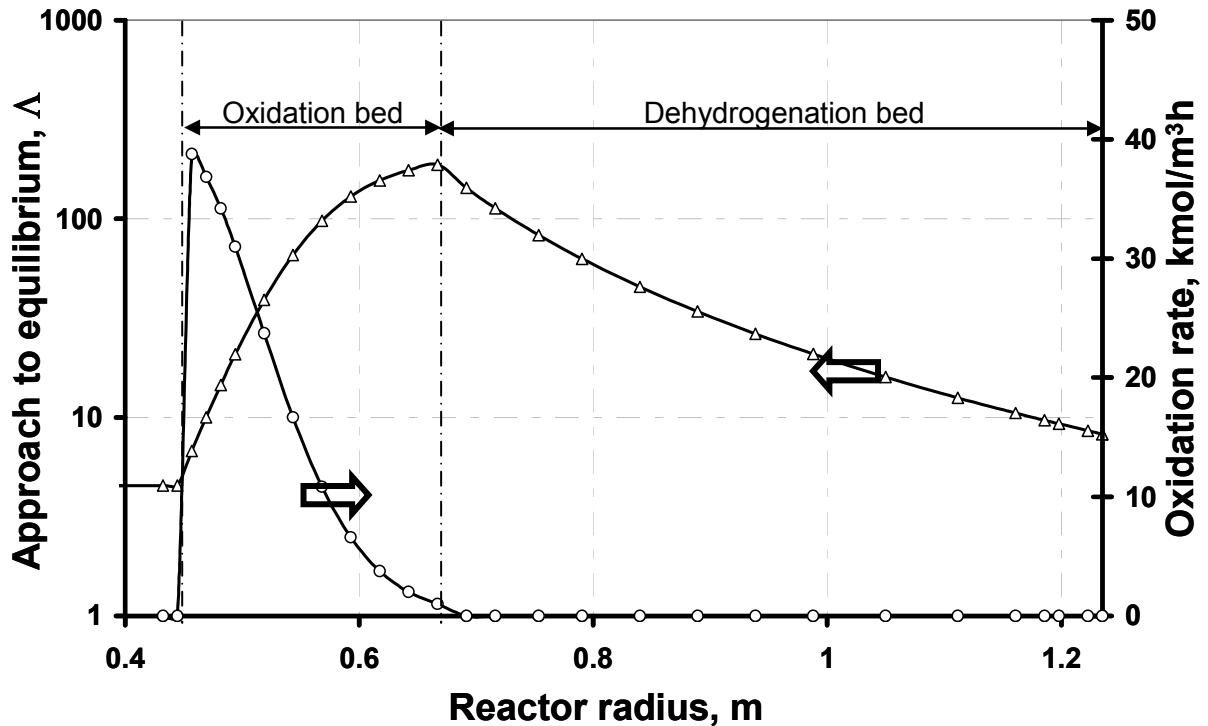


Figure 19: Variation of approach to equilibrium value predicted for the second reactor of SMART process under industrial conditions

It should be noted that oxygen is introduced as a limiting reactant in the second reactor and all oxygen is essentially exhausted in the oxidation bed (Figure 19). Under these conditions, it is obvious that oxidation catalyst distribution should be limited to that part of the reactor where oxygen is present. The simulation studies were carried out by dividing the reactor into multiple zones, typically three, and the ratio of the two catalysts within each zone was varied to arrive at an optimal distribution of the catalysts within the bed. Based on the numerical simulation results, it is apparent that the factors discussed above impose limits on the distribution of the catalyst within reactor and that pellet-scale coupling is not applicable to the entire bed, but is restricted to a layer sandwiched between an oxidation and dehydrogenation catalyst bed alone. Though there is a need for a layer of catalyst, the gain in terms of process conversion by such arrangement is marginal rather than considerable.

Simulation studies were carried out for the SMART process under industrial conditions and for higher Thiele modulus conditions. Figure 19 compares the performance of nearly

optimally distributed “conventional” case against pellet-scale heat coupled case. It is evident from the comparison that gains in terms of conversion by pellet-scale heat integration are rather modest (roughly 2% increase in conversion). As the selectivity of the process is already high (around 96%), the potential improvements in terms of selectivity are also marginal.

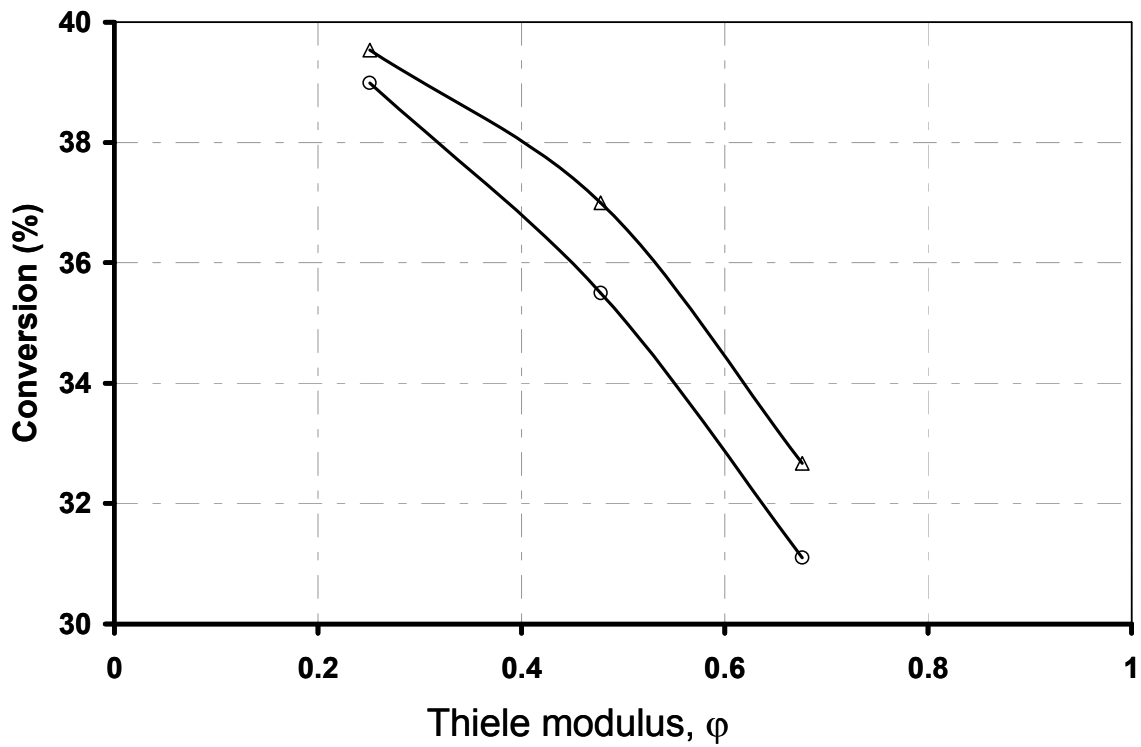


Figure 20: Comparison of conversion in reactor-II for conventional case to pellet scale thermal integrated case.

- △— Particle scale heat integrated case
- Conventional case

## 4.6. Reasons for lacklustre improvement by pellet-scale

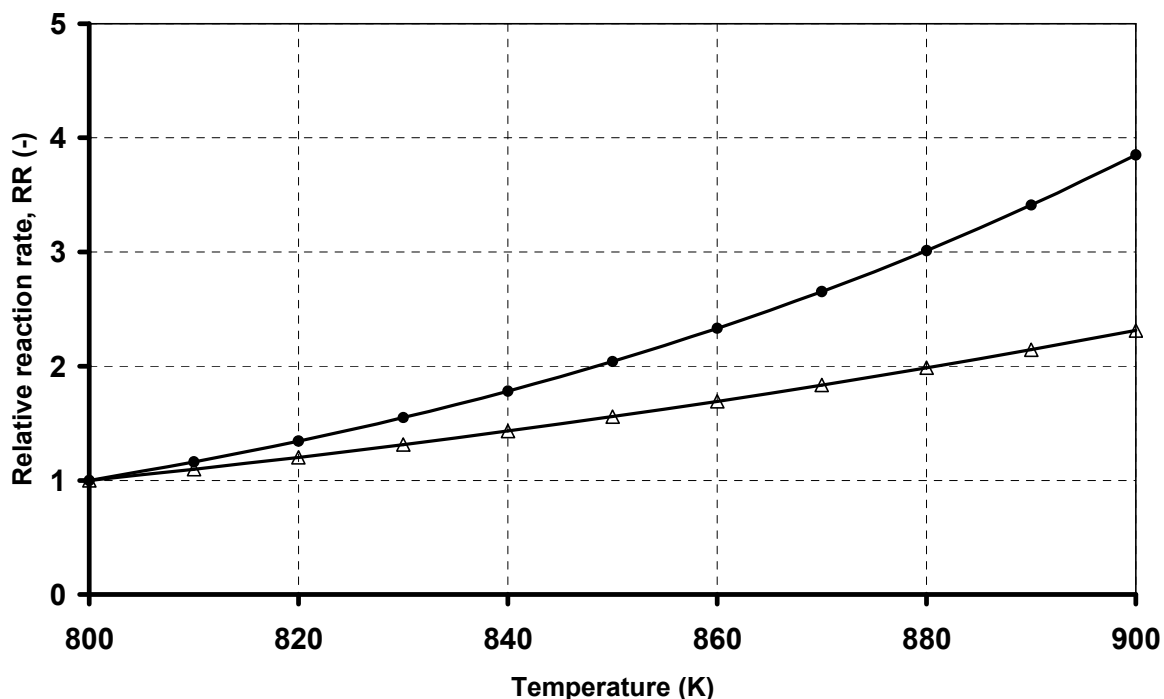


Figure 21: Variation of relative oxidation and ethylbenzene dehydrogenation reaction rate with temperature. 800 K is taken as reference temperature

- Dehydrogenation reaction
- △ Oxidation reaction

Based on the results presented in the previous section, it is obvious that there is very little incentive to entertain the concept of pellet scale heat integration for the SMART process. Before dismissing the concept of heat integration at pellet level as non-functional and pointless, one needs to understand the cause of its failure, so that appropriate alternative applications, if any, may be identified. In this section, we highlight three reasons for the marginal improvement in performance for the SMART process:

- the layer sandwiched between the oxidation and dehydrogenation catalyst was generally only 20% of the total reactor volume and thus had a limited impact on the overall performance of the reactor.
- the primary motivation of integration at pellet level is to de-bottleneck any transport limitations within pellet. As indicated by Weisz-Prater number, the transport limitations in the case of SMART process are not significant and under these conditions, the role of any de-bottlenecking concept is only slight. Figure 22

shows the bulk and pellet temperature profiles for the SMART process under industrial conditions. The maximum temperature difference between bulk gas and pellet is around 5 K, indicating only marginal heat transport limitations.

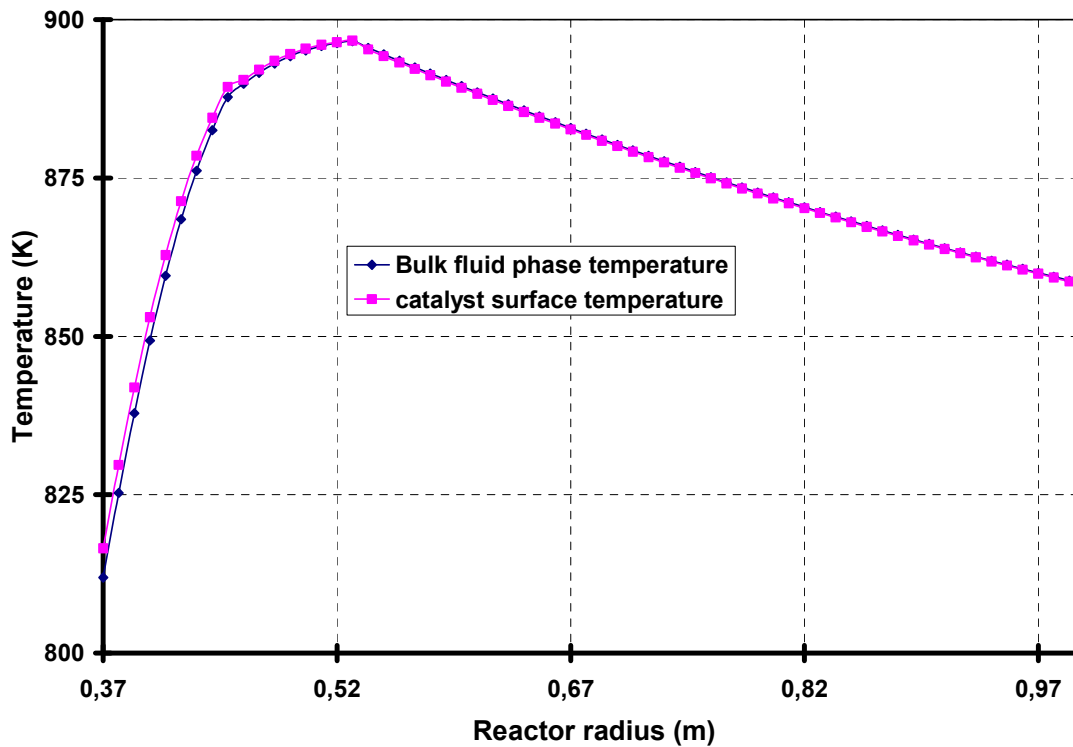


Figure 22: Temperature profile along reactor-II at bulk and within catalyst

- in addition to the role of transport phenomena on the applicability of pellet-scale thermal integration concepts, the intrinsic nature of chemical reaction also plays a role in its performance. The Arrhenius number ( $\frac{E}{RT}$ ) is a measure of the thermal sensitivity of a chemical reaction and its value usually varies from 5 to 30 for typical heterogeneously catalysed reactions. The Arrhenius number for the ethylbenzene dehydrogenation reaction and the hydrogen oxidation reaction are in the range of 6 and, unfortunately, they are both thermally somewhat insensitive. For a 100K increase in temperature, the rate of the reactions increases by a factor of roughly only 3.5 (Figure 21), rendering the concept of pellet-scale heat integration uninteresting for the SMART process.

The above reasoning elucidates the very modest gains achieved by pellet-scale integration in the case of the SMART process.

## 4.7. General applicability of pellet-scale heat integration

Having recognised the conceptual weakness in the applicability of pellet-scale heat coupling for SMART process, the study was extended to identify the conditions under which pellet-scale coupling might be truly beneficial. For this purpose, a single catalyst pellet model was developed. The pellet is assumed to catalyse two first order reactions – an exothermic and endothermic one. The pellet experiences a constant bulk concentration and resistance to mass transport is assumed to reside in both the film and the pellet pores. In the case of heat transport, the resistance in the film is assumed to be dominant. The following equations show the mass and energy balance for the catalyst pellet expressed in terms of dimensionless numbers:

$$\frac{d^2 c_i}{dr^2} + \frac{2}{r} \frac{dc_i}{dr} = -9 \sum_k \frac{\Phi_k^2 \exp(-\gamma_k T/T_p)}{\exp(-\gamma_k)} \nu_{i,k} c_i \quad \text{Equation 42}$$

here  $k = \text{endo, exo}$

Boundary Conditions for the pellet phase are:

$$k_{\text{film}} (c_i - c_p) = D_{\text{eff}} \left. \frac{dc_p}{dr} \right|_{r=R_p} \quad \text{Equation 43}$$

$$\left. \frac{dc_p}{dr} \right|_{r=0} = 0 \quad \text{Equation 44}$$

$$\frac{T_p}{T} - 1 = \frac{d_p}{(6k_{\text{film}} c_i)} [r_{\text{avg, k}} \beta_k + r_{\text{avg, k}} \beta_k] \quad \text{Equation 45}$$

where:

$$k_{\text{endo}} = k_{o_{\text{endo}}} e^{(-\gamma_{\text{endo}} T/T_p)}$$

$$k_2 = k_{o_{\text{exo}}} e^{(-\gamma_{\text{exo}} T/T_p)}$$

$$\Phi_{\text{bulk}_{\text{endo}}} = \frac{d_p}{6} \sqrt{\frac{k_{\text{bulk}_{\text{endo}}}}{D_{\text{eff}}}}$$

$$\Phi_{\text{bulk}_{\text{exo}}} = \frac{d_p}{6} \sqrt{\frac{k_{\text{bulk}_{\text{exo}}}}{D_{\text{eff}}}}$$

$$\gamma_{\text{endo}} = -E_{\text{endo}}/RT$$

$$\gamma_{\text{exo}} = -E_{\text{exo}}/RT$$

$$k_{\text{bulk}_{\text{endo}}} = e^{-\gamma_{\text{endo}}}$$

$$k_{\text{bulk}_{\text{exo}}} = e^{-\gamma_{\text{exo}}}$$

$$\text{Bi}_m = \frac{k_{\text{film}} d_p}{2D_{\text{eff}}}$$

$$\beta_{\text{endo}} = \frac{(-\Delta H_{\text{endo}})}{k_{\text{film}} \rho_g C_p a T} \left[ \frac{N_{\text{Pr}}}{N_{\text{Sc}}} \right]^{2/3}$$

$$\beta_{\text{exo}} = \frac{(-\Delta H_{\text{exo}})}{k_{\text{film}} \rho_g C_p a T} \left[ \frac{N_{\text{Pr}}}{N_{\text{Sc}}} \right]^{2/3}$$

$$N_{\text{Pr}} = \frac{C_p \mu}{\lambda}$$

$$N_{\text{Sc}} = \frac{\mu}{\rho_g D}$$

Based on the conclusions drawn in the previous section, it is expected that the performance of heat coupled pellets is determined by the reaction and transport phenomena occurring within catalyst pellet. The reaction and transport phenomenon can be quantified using dimensionless numbers, such as Biot number, Thiele modulus, Prater number and Arrhenius number. The studies have been carried out to analyse the influence of the above parameters on the performance of heat coupled pellets. Figure 23 shows

the typical values of Arrhenius number and Prater number for some common industrial chemical reactions.

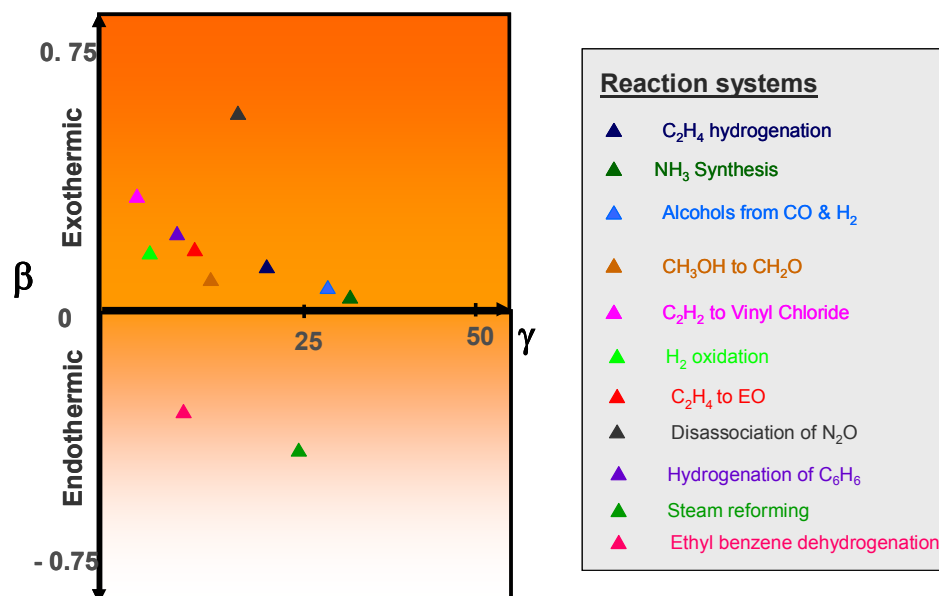


Figure 23: Typical values of Arrhenius number ( $\gamma$ ) and Prater number ( $\beta$ ) for different common industrial reactions

#### 4.7.1. Effect of Arrhenius number

It is known from the standard physical chemistry textbooks that any chemical reaction is distinctly accelerated by thermal energy and the Arrhenius number gives a qualitative indication of the thermal sensitivity characteristics of chemical reactions. Typically, the Arrhenius number varies in the range of 5 to 30 for heterogeneously catalysed reactions. Figure 24 shows the variation of the catalyst effectiveness factor for different values of the Arrhenius number. It is evident that when both the exothermic and endothermic reactions possess low Arrhenius numbers (for example,  $\gamma_{\text{endo}} = 8$  &  $\gamma_{\text{exo}} = 8$  in Figure 24), both the reactions are thermal insensitive and they proceed with little mutual interference. Pellet-scale heat integration is not suitable for such reactions and the SMART process is a classic example of this type of reaction system. For a combination of high Arrhenius number values for endothermic reaction and thermally insensitive exothermic reaction (for example,  $\gamma_{\text{endo}} = 20$  &  $\gamma_{\text{exo}} = 8$  in Figure 24), the heat generated by the exothermic reaction accelerates the endothermic reaction resulting in significant improvements in



catalyst effectiveness factor for the endothermic reaction. It is to be noted that the catalyst effectiveness for endothermic reactions can thus be significantly higher than 1.

If both the participating reactions are thermally sensitive (for example,  $\gamma_{\text{endo}} = 20$  &  $\gamma_{\text{exo}} = 15$  in Figure 24), the heat generation within pellet increases the catalyst effectiveness for the endothermic reaction. The heat consumption by the endothermic reaction lowers the pellet temperature and this lowers the exothermic reaction rate (due to its thermally sensitive nature). For this reasons, the effectiveness of endothermic reaction is not as high as when integrated with a thermally insensitive exothermic reaction.

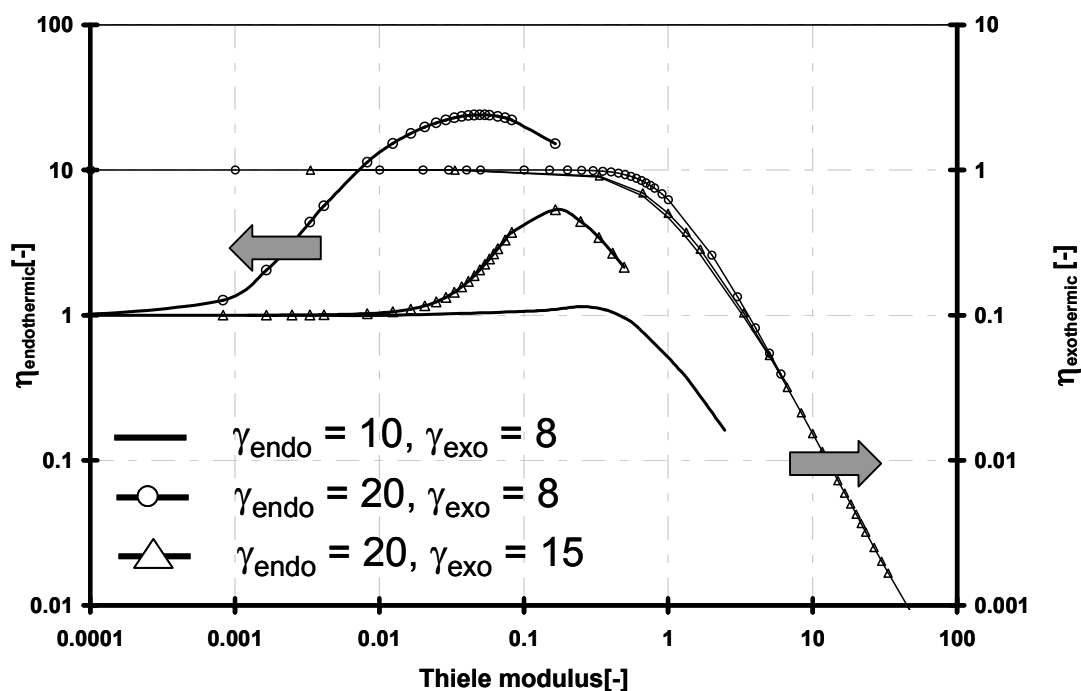


Figure 24: Effect of Arrhenius number on catalyst effectiveness in thermal couple pellets for  $\beta_{\text{exo}} = 0.2$ ,  $\beta_{\text{endo}} = -0.2$

From the above discussions, it is apparent that the thermal sensitivity of the component chemical reactions is crucial for the performance of a pellet-scale heat integrated process. Though it is a necessary condition that the endothermic reaction be thermally sensitive, it is desirable to have a thermally insensitive heat source to achieve significant catalyst effectiveness enhancement for the endothermic reaction.

### 4.7.2. Effect of dimensionless number, $\beta$

The dimensionless number  $\beta$  is analogous to the Prater number and is an indication of the exothermicity or endothermicity of a chemical reaction. One can expect that the heat generation needs to be significant enough to enhance the endothermic reaction. Figure 25 shows the influence of pellet-scale heat integration of exothermic and endothermic reaction for different combinations of  $\beta$ . As expected, a decrease in  $\beta_{\text{exo}}$  lowers the influence of the exothermic reaction on the performance of endothermic reaction and the gains are marginal when  $\beta_{\text{exo}} < \beta_{\text{endo}}$ .

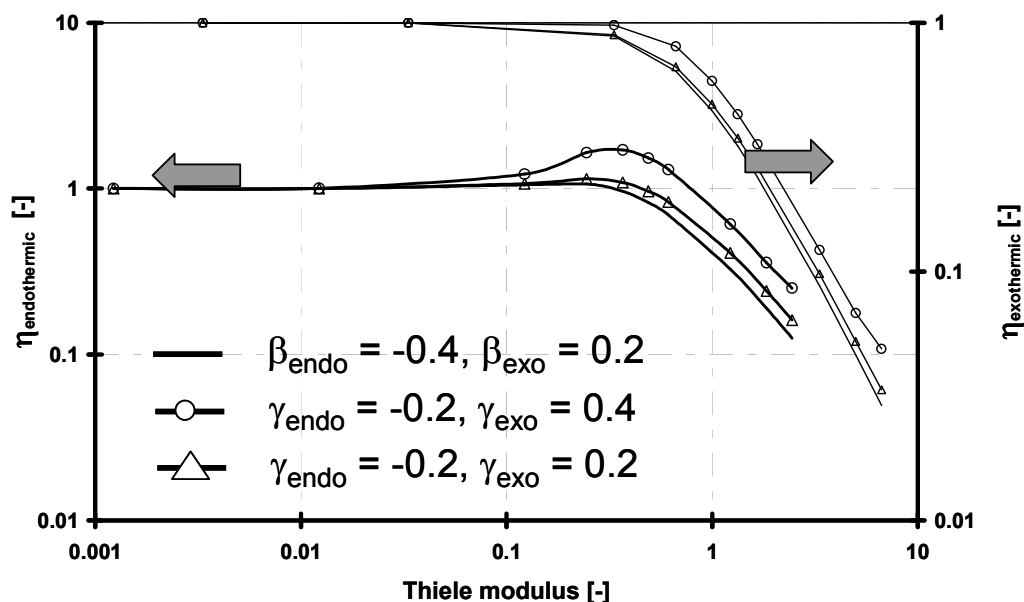


Figure 25: Effect of Prater number on catalyst effectiveness in thermal coupled pellets for  $\gamma_{\text{exo}} = 8$ ,  $\gamma_{\text{endo}} = 10$

### 4.7.3. Effect of mass Biot number ( $Bi_m$ )

It is well-known in reaction engineering that thermal transport limitations set in only in the presence of mass transport limitations. In the absence of film transport limitations, the difference in bulk and pellet temperature is not significant and under these conditions, there is hardly any benefit accrued by pellet-scale reactive heat integration. This is illustrated in Figure 26

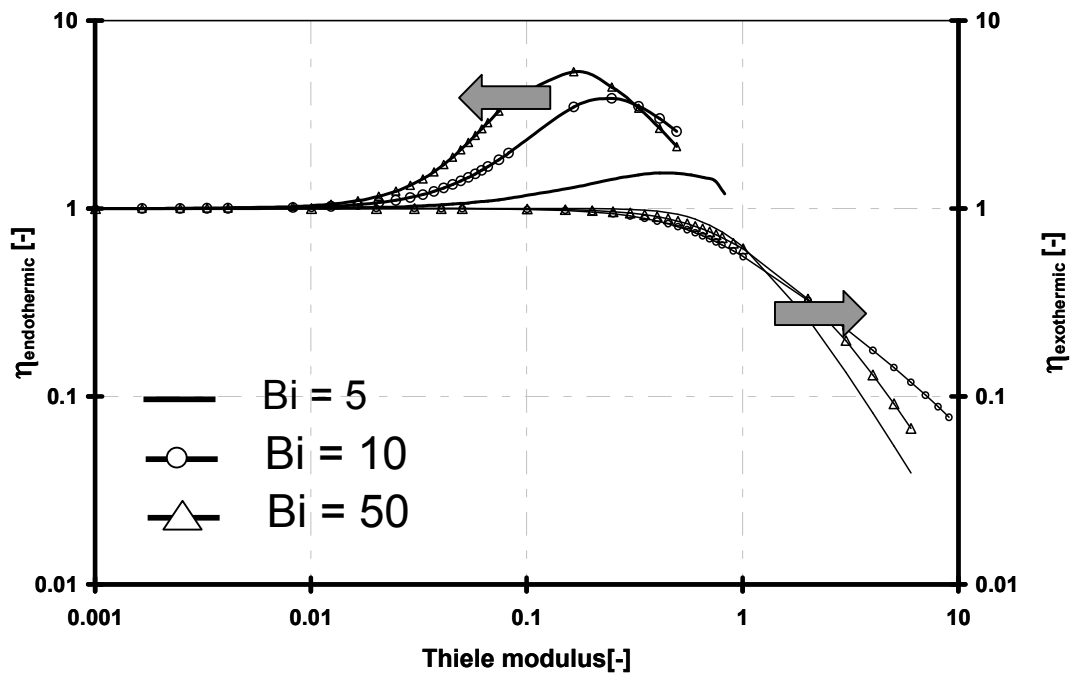


Figure 26: Effect of Biot number on catalyst effectiveness in thermal coupled pellets

## 4.8. Conclusions

In this study, the concept of multifunctional catalysts has been extended to understand the effect of reactive heat coupling within a catalyst pellet. The SMART process, a commercial process to produce ethylbenzene by dehydrogenation, has been taken as the test reaction case to study the performance of this new multifunctional catalyst concept. It has been shown that the dehydrogenation and oxidation are poorly thermally sensitive, which results in only a meagre improvement by using such multifunctional catalysts. Based on a single catalyst pellet model, it has been shown that the thermal sensitivity and the heats of reactions are critical process parameters that can indicate the need for reactive heat coupling at a pellet level. The concept is nevertheless appealingly elegant and new reaction schemes need to be identified to exploit the potential of this concept which has been revealed here.

## **Chapter 5: Summary and future work**

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This work is devoted to understanding the potential available in distributing multiple functionalities within a reactor. Prior to this work, little effort had been expended on identifying the role of functionality distribution in the area of multifunctional reactors, specifically adsorptive reactors, and what little work was carried out in the past lacked systematic rigour. It was against this backdrop that this work was undertaken to generate further insight into this concept and ultimately provide guidelines on how to carry out the structuring of multifunctional reactors.

## 5.1. Structuring in adsorptive reactors

In this part of the work, we have focussed on the structuring potential of adsorptive reactors. Mathematical models of adsorptive reactors were developed and numerical simulation and optimisation studies have been carried out to understand the importance of structuring. Chapter 2 focussed on the importance of structuring at a reactor level and chapter 3 focussed on structuring at a pellet level. Optimisation studies suggest that the distribution of functionalities is chiefly guided by reaction kinetics and process constraints, like the minimum conversion and/or selectivity. In the case of pellet-level structuring, the major gains are achieved by simply integrating the functionalities within a single pellet and further gains by microstructuring of the pellet are minimal. This 'take-home' message is captured in Figure 1, which resembles an optician's chart for testing eyesight and emphasises areas in decreasing importance, that should be considered when designing a multifunctional adsorptive reactor. As highlighted in the chart, macrostructuring is essential to achieve true potential of an adsorptive reactor. Instead of a homogenous distribution of catalyst and adsorbent within the reactor, one needs to analyse the possibility of distributing functionalities non-uniformly to realise full potential of an adsorptive reactor.

From this study, it is apparent that micro-integration is a useful tool for circumventing transport limitations in an adsorptive reactor. It should also be noted that the majority of the gains achieved by microstructuring are achieved simply by integrating the functionalities within a pellet and additional improvements by optimising the distribution of functionalities within a pellet are marginal.

One needs to realise that the optician's chart (Figure 27) has been developed based on the numerical simulations carried out in this work. It should be noted that the validity of the chart is limited by the assumptions that have been used in these simulations and the scope of the work that has been carried out here. Of the various assumptions used in the development of the model, some of the assumptions may influence the optician's chart presented and might potentially alter the hierarchy of importance. The following

discussion highlights the assumptions that need to be considered in any future work to render the chart both generic and comprehensive.

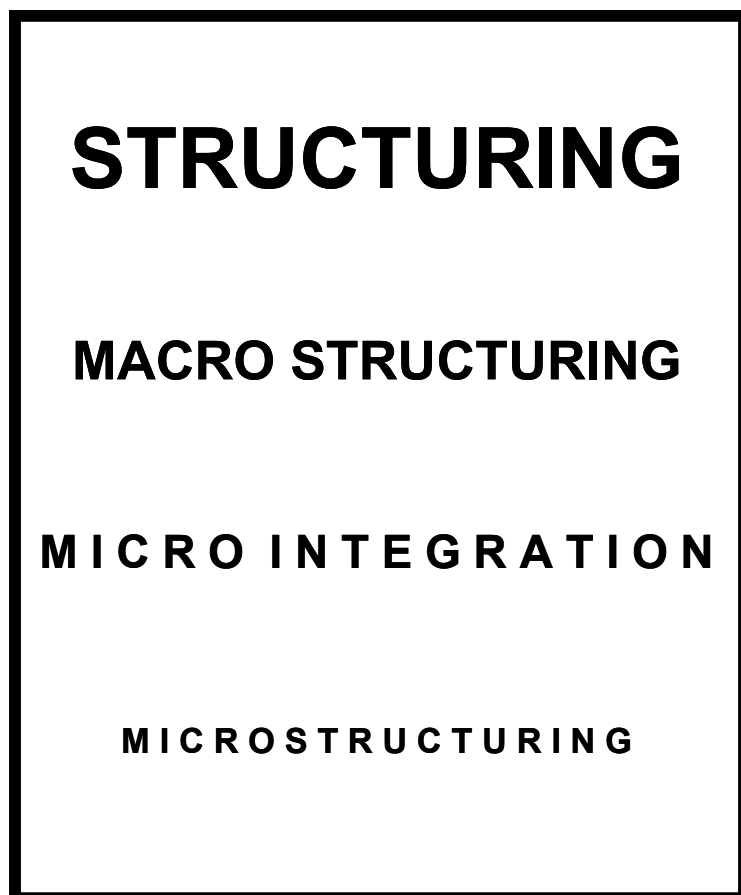


Figure 27: Optician's chart showing the importance of different levels of structuring

### **5.1.1. Non-isothermal adsorptive reactors**

In this work, it has been assumed that the adsorptive reactor operates under isothermal conditions and the heat effects have been neglected. Though this assumption is reasonable for the Claus process conditions, the assumption is not applicable for many other reaction schemes. As adsorption is an exothermic process, the heat liberated during this process may either positively or negatively influence the chemical reactions taking place. In addition, the endothermic or exothermic nature of the chemical reaction can also significantly increase or decrease the adsorbent capacity. Thus, the heat effects of the adsorption and reaction functionality could either be synergistic or counterproductive. As a result, the optimal distribution of the functionalities within an adsorptive reactor can also vary significantly at a reactor and pellet level. For instance,



for an exothermic reaction taking place in an adsorptive reactor, the increase in pellet temperature due to the exothermic nature of the reaction could lead to a lower adsorption capacity and consequently, a segregation of functionalities in separate pellets may well be optimal.

Thus to generalise the study further, it is essential that the heat effects be taken into account and additional effort in this direction is desirable in the future. It should also be noted that this study is limited to reversible reaction schemes such simple reaction schemes seldom correspond to reality. Further studies are required to consider other, more complex, 'real-life' reaction schemes.

### **5.1.2. Diffusion and process cycle time of reaction systems**

In this study, it has been shown that integration of functionalities at a pellet level provides an effective approach to circumvent transport limitations in an adsorptive reactor.

However, as the diffusion time within a pellet ( $\frac{D_{eff}}{R^2}$ ) is very small in comparison to the process cycle time ( $\tau$ ), microstructuring did not yield the process performance gains envisaged. One should note that the diffusion times considered in this study are comparable in magnitude to the values found in commercial catalysts. Thus the results of this study are applicable to any adsorptive reactor using non-zeolite based adsorbents (i.e. adsorbents whose diffusion times are comparable to commercial catalysts). If transport by diffusion is such that the diffusion time is significantly longer than process cycle time (as in zeolite based adsorbents without macropores) or if the process cycle time is small in comparison to diffusion time, it is very likely that optimally microstructured pellet would outperform the simple uniformly distributed multifunctional pellets. Under these conditions, the cycle time would be too small for the pellet to be saturated completely and microstructuring could significantly improve the performance of the process. In addition to the above possibilities, kinetic non-linearities could also result in microstructured pellets outperforming simple uniformly structured multifunctional pellets.

## 5.2. Pellet-scale heat integration

Following the above work on the distribution of adsorbent (mass source/sink) and catalyst functionalities at different levels within a reactor, the concept of de-bottlenecking an endothermic reaction by heat integration with a reactive heat source within the same catalyst pellet was investigated using ethylbenzene dehydrogenation reaction as a test case. The reactive heat source is nothing but an exothermic chemical reaction, which in this case is catalysed by another distinct catalyst. As the heat transport in a catalyst pellet is usually limited by the film surrounding the pellet, the concept of microstructuring is not applicable to this case and hence the work was limited to studying the performance improvement in a simple uniformly distributed multifunctional pellet.

Ethylbenzene dehydrogenation reaction is a highly endothermic, reversible chemical reaction, which is commercially operated by co-feeding large amounts of steam as a heat carrier along with the reactants. UOP's SMART process, which incorporates the oxidation reheat technology has been recently commercialised to produce styrene (the dehydrogenation reaction product) and this process involves the supply of heat for the dehydrogenation reaction by oxidising the hydrogen produced in the same reactor. This reaction was used as a test reaction scheme to study the impact of pellet-scale heat integration on the overall process performance. Disappointingly, the improvement through pellet-scale reactive heat coupling was marginal. It was found that the participating chemical reactions were rather temperature insensitive and reactive heat coupling could not enhance the dehydrogenation reaction. Based on simulation studies carried out on a single catalyst pellet, we found that for the concept of pellet-scale reactive heat coupling to be successful, it is essential that the participating endothermic reaction be thermally sensitive and it is preferable that the exothermic reaction be thermally insensitive. The work on pellet-scale heat integration can be extended further and the following are some of the suggested areas where additional work could be carried out.

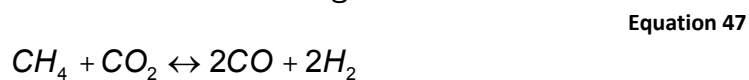
### 5.2.1. Partial oxidation of methane to syngas

The partial oxidation of methane to syngas has been extensively studied as a promising process for the production of syngas due to the favourable H<sub>2</sub> to CO ratio in the product gas as well as the mild exothermicity of the reaction. The reaction is catalysed by Ni/Al<sub>2</sub>O<sub>3</sub> and the steam reforming and oxidation reactions competitively consume the methane present in the system. The following reactions occur during the partial oxidation of methane [Jin, et. al., 2000]

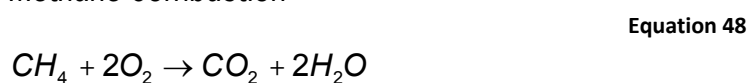
Steam reforming



Carbon dioxide reforming



Methane combustion



It is desirable that the consumption of methane by the combustion reaction is just sufficient to sustain the thermal needs of the reforming reaction. As Ni/Al<sub>2</sub>O<sub>3</sub> catalyses both the exothermic and endothermic reaction, there is little control over the individual reactions and an uncontrolled oxidation reaction can lead to thermal hotspots in the reactor. One may consider altering the residence time of the reactants (for example, introducing oxygen at intermittent locations in the reactor instead of the co-fed mode of operation) to control syngas quality. Alternatively, to have a more localised control over the reactions, one could consider diffusive transportation under the Knudsen regime within catalyst pellets. Under these conditions, the flux is proportional to the square root of the molecular weight of the diffusing component and as steam reforming reactants (CH<sub>4</sub> & H<sub>2</sub>O) have a lower molecular weight than O<sub>2</sub>, they would have a better access to the catalyst site than O<sub>2</sub>, resulting in an enhanced steam reforming reaction. This could

be a potential application where transport limitations play a favourable manipulative role in the reactor.

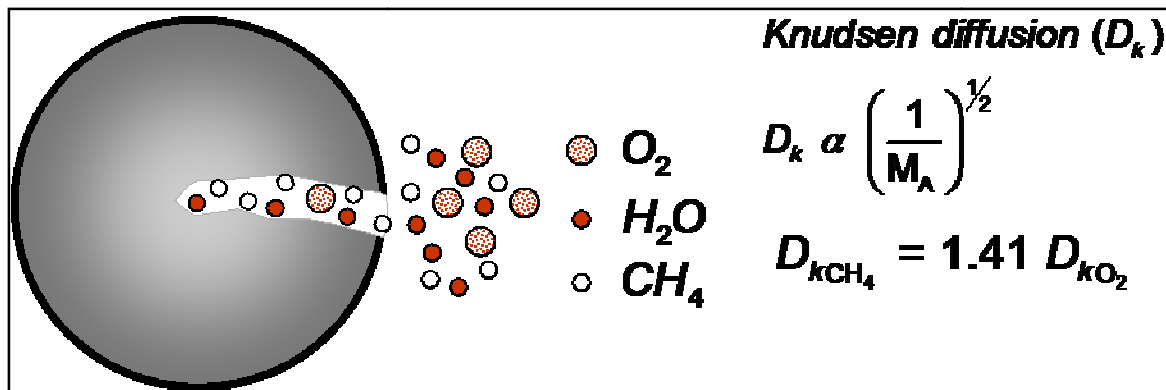


Figure 28: Syngas by partial oxidation of methane under Knudsen diffusion regime

### 5.2.2. Non - reactive pellet-scale heat coupling

In the case of reactive heat coupling, though the combination of an exothermic and endothermic reaction in the same pellet has potential benefits, often the choice of reactions that can be thermally linked in this fashion is limited by their mutual compatibility. At times, the reactants participate in undesirable side-reactions, which could potentially diminish the attractiveness of this concept. One possible approach to overcome this shortcoming, is to consider non-reactive heat source/sinks that could be placed within the catalyst pellets.

Recently, Richrath et. al., [2005] used adsorptive reactors and studied the possibility of controlling the reactor bed temperature by desorbing water vapour during reaction cycle (desorption cycle). Thus, when an exothermic reaction takes place during the reaction cycle, the heat of reaction released supplies the heat of desorption for the adsorbed water and this controls the bed temperature and avoids thermal runaways. The concept is a good example of non-reactive heat coupling in a reactor and microstructuring concepts can be introduced in this case too. A key drawback in this case is the dilution of the process stream by the desorbing coolant, which would potentially necessitate additional downstream processing for separation.

An interesting alternative approach to overcome the above drawback is to consider using phase change materials (PCM) instead of adsorbents. PCMs are high density energy storage materials that can store or release energy within a narrow temperature range. PCMs have already found extensive applications as heat storage materials in solar heating, room heating and similar applications and in general, the applications are limited to the temperature range of 25 to 150°C. Recently, Japanese researchers have exploited the energy storage capacity of PCMs in reaction engineering applications [Maruoka et. al., 2004]. They carried out a feasibility study to recover heat from the intermittent waste gas produced in the steel industry and used this heat to carry out endothermic reactions like steam reforming. Waste heat is available in the temperature range of 1400 – 1700 K and copper (melting point = 1356 K) is chosen as PCM to store heat. Copper balls ( $\cong$  3 mm) are thinly coated with nickel (melting point = 1723 K) using electroplating techniques and are employed in the heat recovery system. This ensures an easy and efficient way of handling PCMs. The report indicates that heat recovery using PCMs is economically viable.

With numerous chemical reactions plagued by either thermal runaway problems or energy deficiency in the case of endothermic reactions, PCMs can potentially be employed to improve the process economics. In addition to a number of elements that melt in the temperature of range of 400 to 800 K, numerous alloys can also be used as PCMs and this provides ample scope for process designers to choose from. Figure 5-3 illustrates the concept of using PCMs as heat sinks in an exothermic reaction system. In addition, one could also envisage catalyst pellet-scale heat coupling in the case of the PCMs. Considering the positive outcome of the feasibility study and the possibility of extending such studies to other areas of reaction engineering, PCMs appear to open extensive opportunities in the area of reaction engineering.

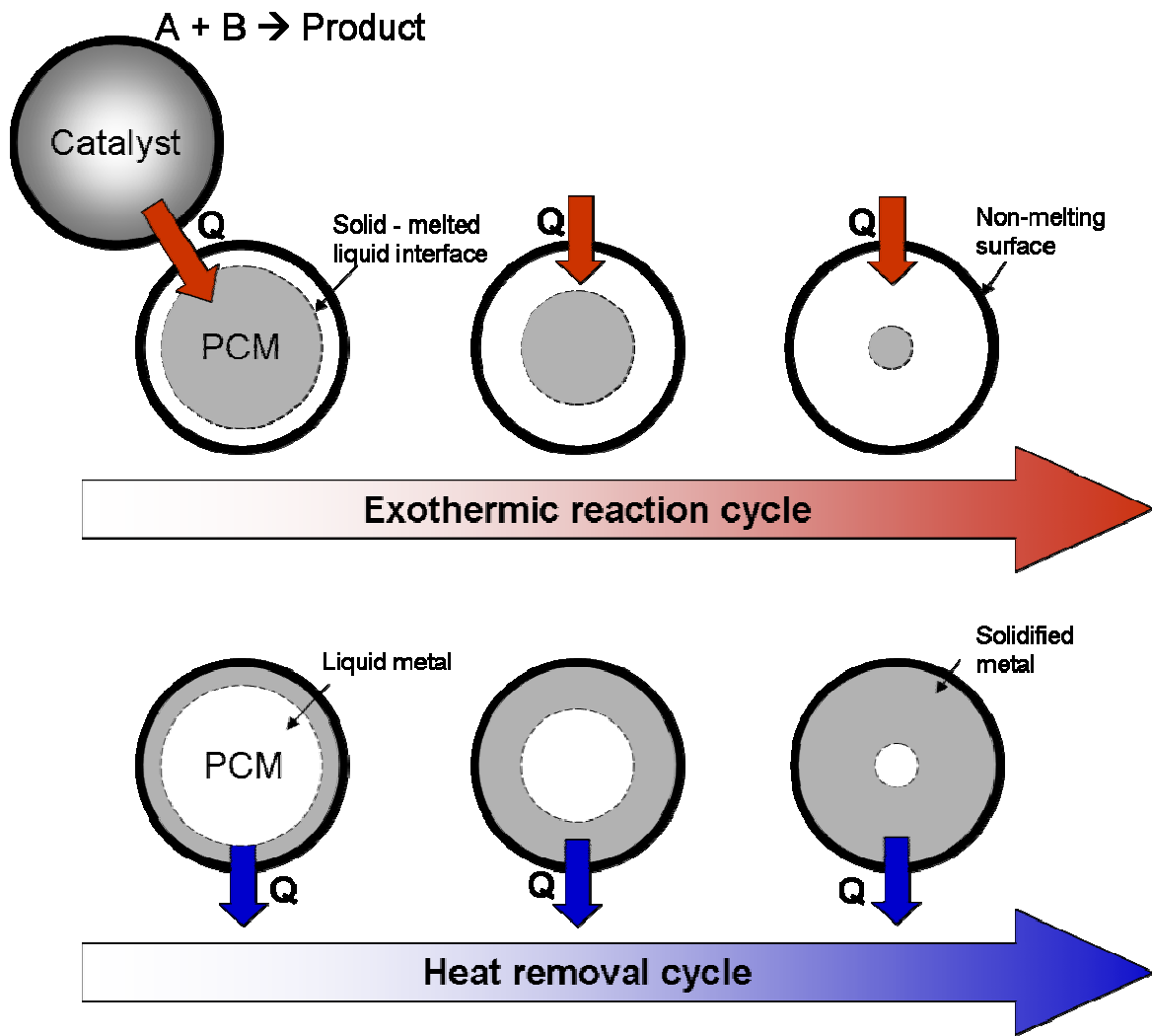


Figure 29: Concept of PCMs as heat sink in reactors

## **5.3. Summary**

To summarise: the distribution of functionalities within a reactor at a pellet and reactor level has been studied. The importance of distribution of functionalities is well understood and some generic guidelines have been developed on the distribution of functionalities. Though good progress has been achieved, there is still a need for considerable research in this field to increase our understanding and to apply the results to novel applications.

# Reference

1. Al-Juhani A.A., Loughlin K.F., Simulation of a combined isomerization reactor and pressure swing adsorption unit. *Adsorption*, 9, 2003, 251 – 264.
2. Agar D. W., Ruppel W., “Multifunktionelle Reaktoren für die heterogene Katalyse”, *Chem. Ing. Tech.* 1988, 60, 731–741.
3. Ahari J.S., Kakavand M., Farshi A., Abedi M. H., “Modelling of radial flow reactors of oxidative reheat process for Production of styrene monomer” *Chem. Eng. Tech.*, 27, 2004, 139-145.
4. Alpay E., Chatsiriwech D., Kershenbaum. L.S., Combined reaction and separation in pressure swing processes, *Chem. Eng. Sci.*, 49, 24B, 5845 – 5864, 1994.
5. Arumugam, B.K., Wankat, P.C., Pressure transients in gas phase adsorptive reactor. *Adsorption* 4, 1998, 345 – 354.
6. Coppens M.O., “The effect of fractal surface roughness on diffusion and reaction in porous catalysts – from fundamentals to practical applications” *Catalysis Today*, 53, 1999, 225 – 243
7. Datsevich L., “Alternating motion of liquid in catalyst pores in a liquid/ liquid – gas reaction with heat or gas production” *Catalysis Today*, 79 – 80, 2003, 341 – 348
8. Datsevich L., “Some theoretical aspects of catalyst behaviour in a catalyst particle at liquid (liquid – gas) reactions with gas production: oscillation motion in catalyst pores” *Appl Catal A–Gen*, 247, 2003, 101-111
9. Dautzenberg F.M., Mukherjee M., “Process intensification using multifunctional reactors”, *Chem. Eng. Sci.*, 56, 251 – 267, 2001.
10. Edgar T.F., Himmelblau D.M., Lasdon L. S., “Optimization in chemical processes”, 2nd edition, McGraw-Hill Chemical engineering series, 2001.
11. Elnashaie S.S.E.H., Elshishini S.S., “Modelling, simulation and optimization of industrial fixed bed catalytic reactors”, (*Topics in chemical engineering; v. 7*), Gordon and Breach Science Publishers S.A., 1993.
12. Elsner M.P., Dittrich C., Agar D.W., Adsorptive reactors for enhancing equilibrium gas-phase reactions – Two case studies, *Chem Eng. Sci.* 57 (9), 1607, 2002



13. Elsner M.P., Menge M., Müller C., Agar D.W., "The Claus process: teaching an old dog new tricks", *Catalysis Today*, 79 – 80, 2003, 487 – 494.
14. Elsner, M.P; "Experimentelle und modellbasierte Studien zur Bewertung des adsorptiven Reaktorkonzeptes am Beispiel der Claus-Reaktion" Ph.D. Dissertation, University of Dortmund, 2004.
15. Ehrfeld W., Hessel V., Haverkamp V., "Micro reactors", *Ullmann's Encyclopaedia of Industrial chemistry*, 1999
16. Foley H.C., "Catalyst preparation – design and synthesis" *Catalysis Today*, 22, 1994, 235 – 260
17. Gheorghiu S., Coppens M.O., "Optimal bimodal pore networks for heterogenous catalysis", *AIChE J.*, 50, 4, 2004, 813 – 820.
18. Gray B. F., Ball R., "Thermal stabilization of chemical reactors-I The mathematical description of Endex reactor" *Proc. R. Soc. Lond. A*, 455, 163 – 182, 1999.
19. Hamel C., Thomas S., Schädlich K., Seidel-Morgenstern A., "Theoretical analysis of reactant dosing concepts to perform parallel-series reactions", *Chem. Eng. Sci.*, 58, 2003, 4483-4492.
20. Hanisch C. (2003), "Surprising Symbiosis", Siemens webzine - Pictures of the Future, Spring 2003. [http://w4.siemens.de/Ful/en/archiv/pof/heft1\\_03/artikel04/](http://w4.siemens.de/Ful/en/archiv/pof/heft1_03/artikel04/)
21. Hegedus L.L., *Catalyst Design: Progress and Perspectives*, John Wiley & Sons, 1 edition, 1987
22. Hoiberg. J.A., Clych.B, Foss.A.S. *AIChE J.* 1434, 1971.
23. Hufton, J.R., Mayorga. S., Sircar. S., Sorption-enhanced reaction process for hydrogen production. *AIChE J*, 1999, 45, 2, 248 – 255.
24. Kahnis H., Wernke R., Grünewald M., Agar D.W., "Periodic reactor operation for enhancement of mass transfer in porous catalyst particles" Submitted for publication
25. Keil F.J., "Diffusion and reaction in porous networks", *Catalysis Today* 53, 1999, 245 – 258
26. Keil F.J., "Modelling of phenomena within catalyst particles", *Chem. Eng. Sci.*, 51, 10, 1543 – 1567, 1996

27. Kekoe J. P. G., Butt J. B., "Interactions of inter- and intraphase gradients in a diffusion-limited catalytic reaction" *A. I.Ch. E. Journal*, 18, 2, 347-355, 1972.
28. Kestenbaum H., de Oliveira A. L., Schmidt W., Schuth F., Ehrfeld W., Gebauer K., Lowe H., Richter T., Lebiecz D., Untiedt I., Zuchner H., "Silver-catalysed oxidation of ethylene to ethylene oxide in a microreaction system", *Ind. Eng. Chem. Res.*, 2002, 41, 710 – 719.
29. Klose F., Wolff T., Thomas S., Seidel-Morgenstern A., "Concentration and residence time effects in packed-bed membrane reactors", *Catalysis Today*, 82, 2003, 25-40.
30. Kodde A. J., Fokma Y. S., Blik A., "Selectivity effects on series of reactions by reactant storage and PSA operation", *AIChE J*, 2000, 46, 11, 2295 - 2304.
31. Kolios G., Eigenberger G., "Styrene synthesis in a reverse-flow reactor", *Chem. Eng. Sci.*, 54(15/17), 2637-2646, 1999
32. Kolios G., Frauhammer J., Eigenberger G., "Autothermal fixed-bed reactor concepts" *Chem. Eng. Sci.*, 55, 5945 – 5967, 2000
33. Krishna R., Sie S.T., "Strategies for multiphase reactor selection", *Chem. Eng. Sci.*, 49, 24A, 4029-4065, 1994.
34. Lawrence P.S., Grünwald M., Agar D.W., Optimal distribution of functionalities in an adsorptive reactor, *Ind. Eng. Chem. Res.*, 2006, 45 (14), pp 4911–4917.
35. Lee I.D., Kadlec R.H., "Effects of adsorbent and catalyst distributions in pressure swing reactor", 167-176, 264, Vol. 84, *AIChE Symposium series*, 1984.
36. Lu Z. P., and Rodrigues A. E., "Pressure swing adsorption reactors: Simulation of three-step one-bed process" *AIChE J*, 40, 1994, 1118 – 1137.
37. Lummus/UOP SMART SM process: <http://www.uop.com/objects/Smart%20SM.PDF>
38. Mann R., "Developments in chemical reaction engineering: Issues relating to particle pore structures and porous materials", *Trans IChemE*, 71, Part A, 1993, 551- 562
39. Mann R., Al-Hamy A., Holt A., "Visualised porosimetry for pore structure characterisation of a nickel/alumina reforming catalyst", *Trans IChemE*, 73, Part A, 1995, 147- 153

40. Maruoka N., Mizuochi T., Purwanto H., Akiyama T., "Feasibility study for recovering waste heat in the steelmaking industry using a chemical recuperator", *ISIJ International*, 44(2), 257-262, 2004.
41. McCabe W.L., Smith J., Harriot P., "Unit operations of chemical engineering" McGraw-Hill International edition, 1993
42. Morbidelli M; Servida A ; Varma A., "Optimal catalyst activity profiles in pellets 1. The case of negligible external mass transfer resistance", *Ind. Eng. Chem. Fundam*, 21, 278 – 284, 1982
43. Motal R.J., O'Rear D.J., "Protection of Fischer-Tropsch catalysts from traces of sulphur" US Patent No. 6,682,711, 2004.
44. Ng K. L., Chadwick D., Toseland B. A., "Kinetics and Modelling of One-stage Synthesis of Dimethyl Ether from Synthesis Gas", *Chem. Eng. Sci.*, 54, 3587-3592, 1999.
45. Park SE, Han SC, "Catalytic dehydrogenation of alkylaromatics with carbon dioxide as a soft oxidant", *J. Ind. Eng. Chem.*, 10 (7): 1257-1269 DEC 2004
46. Ressler S., Agar D.W., Enhancement of the Syngas-to-Dimethyl Ether Process by Adsorptive Water Removal, Poster presentation, 4th Int. Symp. on Multifunctional Reactors, Portoroz – Portorose, Slovenia, June 15 – 18, June 2005.
47. Richrath M, Grunewald M, Agar DW, "Temperature control at the particle level by coupling of reaction and desorption - Part 1", *Chem.-Ing.-Tech* 77 (1-2): 94-101, JAN 2005.
48. Sie S.T, Krishna R., „Process Development and Scale up: Catalyst design strategy“ *Rev. Chem. Eng.*, 14, 3, 159-201, 1998.
49. Stitt E.H., "Multifunctional reactors? 'Up to a point Lord Copper'", *Chem. Eng. Res. Des.*, 82(A2): 129-139, 2004
50. Strano M. S., Foley H. C., "Modeling ideal selectivity variation in nanoporous membranes" *Chem. Eng. Sci.*, 58, 2003, 2745 – 2758
51. TA Luft, Deutschland, Nr. 2.5.1, 1986
52. Wakao, N., Funazkri, L.T., "Effect of fluid dispersion coefficients on particle-to-fluid mass transfer coefficients in packed beds" *Chem. Eng. Sci.* 33, 1375-1384, 1978.

53. Weisz, P. B. Polyfunctional Heterogeneous Catalysis. In Advances in Catalysis and Related Subjects; Eley, D. D., Selwood, P. W., Weisz, P. B., Eds.; Academic: New York, 1962, 137.
54. H. Kahnis, R. Wernke, M. Grünwald, D. W. Agar "Instationäre Druckführung zur Verbesserung des Stofftransports in porösen Katalysatorpartikeln" Chem. Ing. Tech. 76 (2004), 1302-1304
55. Xiu G.H., Li P., Rodrigues A.E., New generalized strategy for improving sorption-enhanced reaction process, Chem. Eng. Sci., 58, 2003, 3425 – 3437.
56. Xiu G.H., Rodrigues A.E., "Sorption enhanced reaction process with reactive regeneration" Chem. Eng. Sci., 57, 3893 – 3908, 2002
57. Yang R. T., Gas separation by adsorption processes, Series of Chemical engineering, Vol –I, Imperial College Press, 1997.
58. Yongsunthon, I., Alpay, E., "Design of periodic adsorptive reactors for the optimal integration of reaction, separation and heat exchange" Chem. Eng. Sci., 54, 1999, 2647 – 2657
59. Zirkwa I, Wernke R, Grünwald M, „Intensification of mass transfer in heterogeneous catalytic reactions by pressure oscillation" Chem.-Ing.-Tech, 76, 7, 955-961, 2004

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