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Spatial distribution of functionalities in an adsorptive reactor at the particle level

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Abstract

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. Transport resistances affect the performance of adsorptive reactors adversely and the integration of functionalities within the same particle circumvents this limitation. Instead of a simple uniform integration of functionalities within the particle, one can also non-uniformly distribute the functionalities over the particle to exploit the concentration profiles arising from transport limitations for process enhancement. A detailed numerical investigation has been carried out to identify the optimal distribution of catalyst and adsorbent functionalities at a particle and reactor level using Aspen Custom Modeler. Though process enhancements are possible by non-uniform distribution within particle, the benefits are marginal. Nevertheless, the integration of functionalities within a particle offers significant improvements in adsorptive process performance.

Keywords: Adsorptive reactor; Claus process; Microstructuring; Functionality distribution; Multifunctional reactor

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 [1,2]. The Claus process [3], total isomerisation process [4], HCN synthesis [3] and dehydrogenation of methyl cyclohexane [5] are some of the other reaction schemes which have been studied in the context of adsorptive reactors. Ng et al. [6] 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 [7].

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. An expedient distribution of adsorbent (and catalyst) along the adsorptive reactor has been found to improve the performance of adsorptive reactor and the utilisation of the functionalities. For the Claus process, Elsner et al. [3] show the existence of an optimal uniform catalyst to adsorbent mass ratio along the axial reactor length to maximise the breakthrough time of the unconverted reactant. For sorption enhanced steam reforming, a reactor with three-subsections, each with a varying mass ratio of adsorbent to catalyst to improve the reactor performance has been proposed [1]. Though an improved

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Nomenclature

c_i	bulk phase concentration (mol/m^3)
c_0	concentration of reactant at reactor entrance (mol/m^3)
c_p	particle concentration (mol/m^3)
d_p	particle diameter (m)
D	reactor diameter (m)
D_i	molecular diffusion coefficient (m^2/s)
D_{ax}	axial dispersion coefficient (m^2/s)
$D_{eff,i}$	effective pore diffusion coefficient $D_{eff} = D_i\varepsilon_p/\text{tau}$ (m^2/s)
f_{ads}	adsorbent particle fraction in conventional reactor
f_{cat}	catalyst particle fraction in conventional reactor
k_1	forward reaction rate constant, Claus reaction (mol/bar$^{1.17}$ m^3 s)
k_2	reverse reaction rate constant, Claus reaction (mol/bar$^{0.99}$ m^3 s)
k_{film}	external particle mass transfer coefficient (m/s)
l_p	characteristic particle length (m)
L	reactor length (m)
p_i	partial pressure of reacting species (bar)
P	reactor pressure (bar)
r	radial coordinate (m)
r_i	radial coordinate (m)
$r_{V,ads}$	adsorption rate (mol/m^3 s)
$r_{V,cat}$	reaction rate (mol/m^3 s)
R_p	particle radius (m)
t	time (h)
tau	particle tortuosity factor
T	reactor temperature (K)
u	superficial gas velocity (m/s)
x	axial coordinate (m)
X	reaction conversion

Greek letters

ε	reactor void fraction
ε_p	particle porosity
τ	cycle time (h)
Λ	approach to equilibrium
Φ	Thiele modulus

Subscripts

ads	adsorbent particle
cat	catalyst particle
min	minimum
i	reactor section number
j	particle layer number

performance is claimed in combination with temperature profiling, little information is provided on the basis for selecting different distributions and the choice seems arbitrary. Recently, we have demonstrated the importance of spatial distribution of functionalities in adsorptive reactors at the reactor level [8]. 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 widen the adsorbate concentration front and thus worsen the performance. One possible solution to circumvent transport limitations is to combine the functionalities within the same particle. By integrating the functionalities in this manner, they are brought into closer proximity with one another, reducing the unfavourable influence of transport limitations.

For the distribution of a single catalytic activity within a particle, Morbidelli et al. [9] have shown that transport limitations are not always detrimental to process performance and that by prudent distribution of catalyst activity within a particle, 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 particle level is necessary. With only limited knowledge of underlying microstructured functionalities, one can propose a range of possibilities for distributing the functionalities within a particle optimally, ranging from a uniform distribution to complete segregation of functionalities (Fig. 1). In this article, we shall analyse the benefits of non-uniformly distributing the functionalities within the particle space and study the possible improvements achieved by this microstructuring of adsorptive reactors. For the sake of clarity, the concept of particle level distribution is subsequently referred to as microstructuring. The single stage Claus process, an adsorptive reactor concept proposed previously by our group [3] was chosen as the base case for this study. The model parameters required were obtained from published data [3,10] or calculated using empirical correlations and are summarised in Table 1.

2. Modelling

A two-phase heterogeneous dispersion model with internal pore diffusion describing the dynamic behaviour of a fixed-bed adsorptive reactor with microstructured particles has been developed. The studies were carried out under isothermal conditions. A detailed discussion of the reactor model and the assumptions involved is provided elsewhere [8]. Only the particle and reactor mass balance equations will be reiterated briefly here.

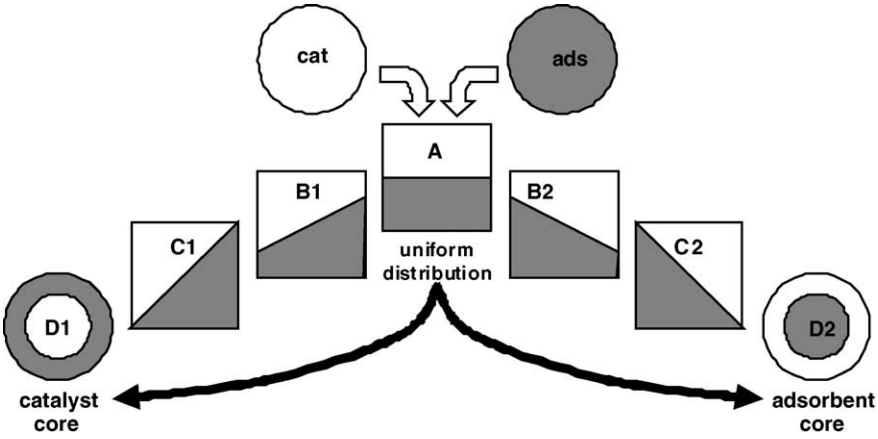

Fig. 1. Microstructuring of functionalities: homogenisation or segregation of functionalities within a particle.

Table 1
Model parameters and correlations used in the study

ε	0.4
ε_p	0.5
D_i (m^2/h)	0.2
L (m)	1.5
u (m/s)	0.15–0.30
T (°C)	225
P (bar)	1.013
d_p (mm)	2–10
D (m)	0.06
k_{film} and D_{ax}	Wakao and Funazkri [11]

Component	Inlet composition (bar)
p_{H_2S}	0.1
p_{SO_2}	0.05
p_{N_2}	0.85

Inside the particles 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 particle volume element resulting in the following expression for the particle mass balance (1):

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

The particle models are incorporated in a fixed-bed reactor and a one-dimensional axial dispersion model is used to describe the reactor fluid bulk phase (2). The third term on the right hand side of Eq. (2) accounts for the mass transfer from the fluid bulk phase to the microstructured particle.

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

3. Optimisation procedure

As will be explained later, at any time, different sections of an adsorptive reactor tend to be dominated either by the reaction kinetics or sorption processes. This suggests that the optimal microstructure for a reactor is not unique, but rather may differ with axial position within reactor. Thus to arrive at an optimal microstructure, the microstructure optimisation study cannot be considered in isolation, but warrants a simultaneous optimisation at the reactor and particle level. For this reason, the optimisation space is divided into discrete elements and the optimal functionality distribution in each element is determined.

Though it is desirable to arrive at a continuous optimal functionality distribution profile along the reactor length and within particle, the problem is simplified by a discrete approach, which yields entirely adequate results. 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 length has been divided up into 13 discrete sections and in each section, the particle has been divided up into five layers (Fig. 2). Within any discrete element, the optimiser is given the freedom to choose the fraction of catalyst/adsorbent, subject to process constraints. The definition of the optimisation criteria are thus as follows:

Objective function: Maximum process cycle time, τ.
Variable constraints:

$$0 < f_{cat_{i,j}} < 1$$

$$f_{cat_{i,j}} + f_{ads_{i,j}} = 1$$

where $i = 1, 2, 3, \ldots, 13$ (segment number); $j = 1, 2, \ldots, 5$ (layer number).
Process constraints: Actual conversion, $X(t) \geq$ desired minimum conversion, X_{min}.

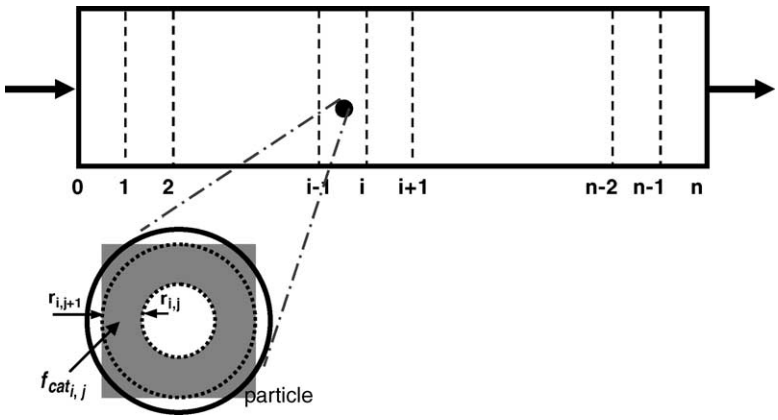

Fig. 2. Scheme for the optimal distribution of functionalities in adsorptive reactor at a particle and reactor level. The notation $r_{i,j}$ indicates the radius of the particle located at the ith segment of reactor and jth layer within the particle. The fraction of catalyst at this location is indicated by $f_{\mathrm{cat}_{i,j}}$.

For any given reactor length and feed flow rate conditions, the 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. For the Claus process, the desired conversion is set by environmental legislation, which typically demands a minimum sulphur recovery of 99.5% (German environmental standards [12]).

Dynamic simulation studies have been carried out using Aspen Custom Modeler® (ACM), while the feasible path successive quadratic programming optimiser, FEASOPT®, which is part of the ACM packet, 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 variable (cycle time) at the current point and moves the design variables (catalyst fraction values) to take the objective variable towards its optimum value. After solving with the new values of the design variables, FEASOPT® re-evaluates the objective variable. 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.

4. Results and discussion

As adsorptive reactors are operated under unsteady state conditions, all catalyst and adsorbent particles are subjected to continuously varying reactant and product concentrations throughout the process cycle and this complicates the task of identifying the optimal microstructure within particle. To simplify this task, one needs to discern the different regimes that influence the performance of an adsorptive reactor. The approach to equilibrium (Λ) 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:

$$\Lambda = \frac{\prod_i c_i^{\upsilon_i}}{K_{\mathrm{eq}}} = \frac{p_{\mathrm{H_2S}}^{0.95}\, p_{\mathrm{SO_2}}^{0.22}}{p_{\mathrm{H_2O}}^{0.99}}\, \frac{k_1}{k_2} \tag{3}$$

for $\Lambda = 1$, the reaction is at thermodynamic equilibrium; $\Lambda > 1$, forward reaction occurs; $\Lambda < 1$, backward reaction occurs.

The right hand side of Eq. (3) is based on the empirical kinetic expression for the Claus process [3,10].

Fig. 3 shows the typical variation of Λ along the length of an adsorptive reactor at different cycle times before the process constraint is breached. The figure indicates that the value of Λ 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 three 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 ($u = 0.3$ m/s, $R_{\mathrm{p}} = 7$ mm) are discussed here for

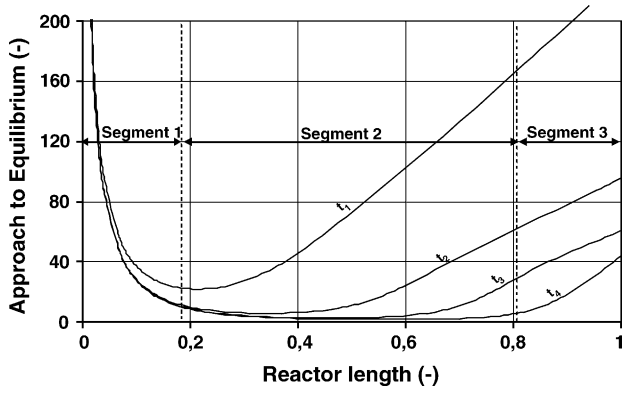

Fig. 3. Typical variation of approach to equilibrium Λ along the axial space at different process times for the Claus process ($R_{\mathrm{p}} = 7$ mm, $u = 0.25$ m/s). Here $t_1 < t_2 < t_3 < t_4$.

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 as the reference value offers one the possibility to compare the relative amounts of H_2S and H_2O present at any point within reactor. The normalised concentration is defined as follows:

$$c_{\text{comp}}(r,t) = \frac{c_{\text{comp}}(r,t)}{c_{\text{H}_2\text{S, inlet}}} \quad (4)$$

4.1. Segment 1

In this segment, the value of Λ is always greater than one and is virtually constant with time. The positive value of Λ 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. Fig. 4 shows the concentration profile of H_2S (reactant) and H_2O (adsorbate) within a microstructured particle located in this segment at different process times. The reactant concentration profile undergoes little evolution with time and 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. [9], for simple power law kinetics, one can expect that a catalyst shell arrangement would offer the optimal performance. The shaded area in Fig. 4 shows the optimal fraction of catalyst in microstructure recommended by the optimiser and the structure closely resembles a catalyst shell arrangement.

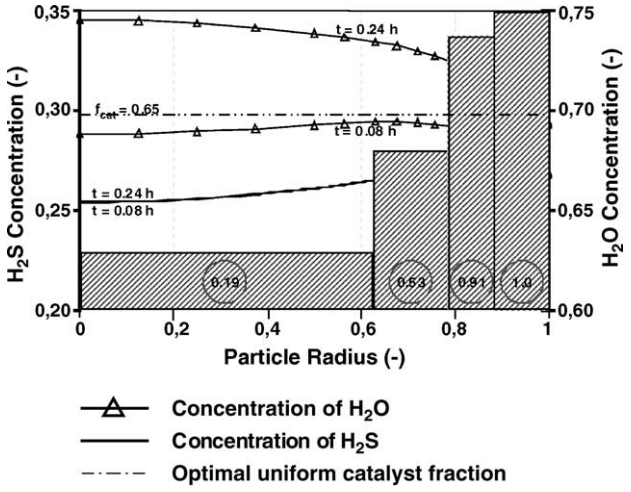

Fig. 4. H_2S and H_2O concentration profile within a microstructured particle located 135 mm from reactor entrance. The shaded areas and the circled numbers indicate the optimal catalyst fraction at any location within particle.

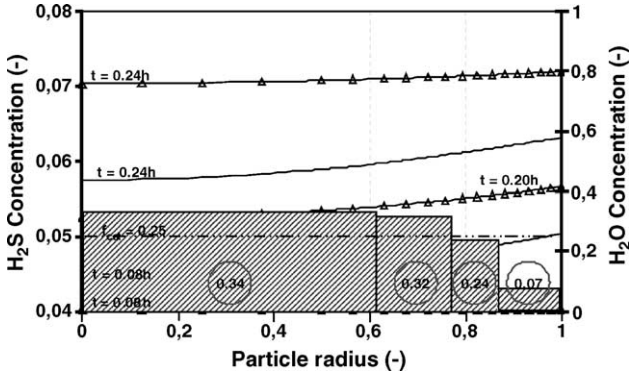

Fig. 5. H_2S and H_2O concentration profile and optimal microstructure within a microstructured particle located at 675 mm from reactor entrance. Refer Fig. 4 for legend.

4.2. Segment 2

Unlike the previous segment, this segment is characterised by a dynamic variation of Λ with space and time (Fig. 3). At any point, while the adsorbent is unsaturated, Λ is greater than one. Upon adsorbent saturation, however, the value of Λ reaches one and this indicates the approach to reaction equilibrium. Thus, though the segment is initially kinetically controlled, the sorption regime gradually sets in. Fig. 5 illustrates the concentration profile of H_2S (reactant) and H_2O (adsorptive) within a microstructured particle located in this segment at different process times.

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 Fig. 5 shows the optimal microstructure of the particle 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 particle tends to be rather uniform. The high adsorbent fraction in the particle shell is attributed to the importance of adsorptive removal to sustain the forward reaction.

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

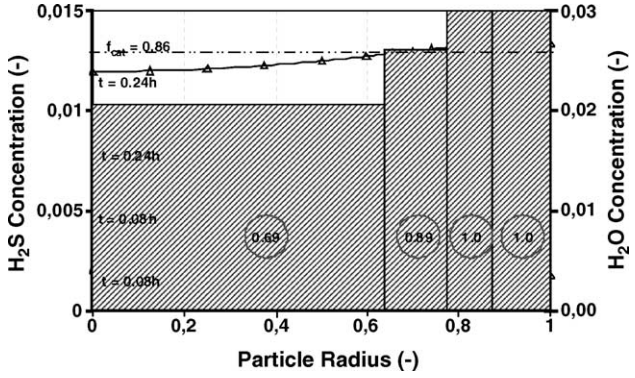

Fig. 6. H_2S and H_2O concentration profile and optimal microstructure within a microstructured particle located at 1335 mm from reactor entrance. Refer Fig. 4 for legend.

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. Fig. 6 shows the concentration profile of H_2S (reactant) and H_2O (adsorbate) within a microstructured particle 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.

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 [1].

5. Relevance of microstructuring

From the previous discussion, it is obvious that the choice of particle microstructure is unique to the regime that governs the particle behaviour. In order to study the importance of the non-uniform distribution of functionalities within particle, an additional optimisation run for the above test case was carried out with only one particle layer (i.e., a uniform particle distribution case), while the same number of axial discrete sections was retained. The broken lines in Figs. 4–6 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 particle level integration of functionalities can perform as well as any optimal microstructure and the marginal difference in performance is attributable to the following causes:

1. In general, the combined width of segments 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.
2. The optimal microstructure in segment 2 is not far from a uniform distribution of functionalities within a particle anyway. Furthermore, segment 2 occupies a major portion of the total bed length and thus exerts a significant influence on the overall reactor performance.

6. Realities of microstructuring

All of the above observations indicate the limitations on the application of microstructuring to the Claus process. But can the microstructuring of adsorptive reactors ever be a useful concept for other adsorptive reaction systems? The answer to this question may be found by comparing the typical diffusion time constants in a particle to the process cycle times. The diffusion time is defined as the time needed by a molecule at the particle surface to diffuse into the particle (of the order of R_p^2/D_{eff}). Typical diffusion times for gas phase systems are in the range of 0.01–2 s. In comparison to the relatively small diffusion times, the process cycle times are significantly higher (of the order of minutes) and thus provide ample time for the diffusion to take place leaving the system lacking 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 process behaviour. If the diffusion time constants and the process cycle time were to be comparable, then

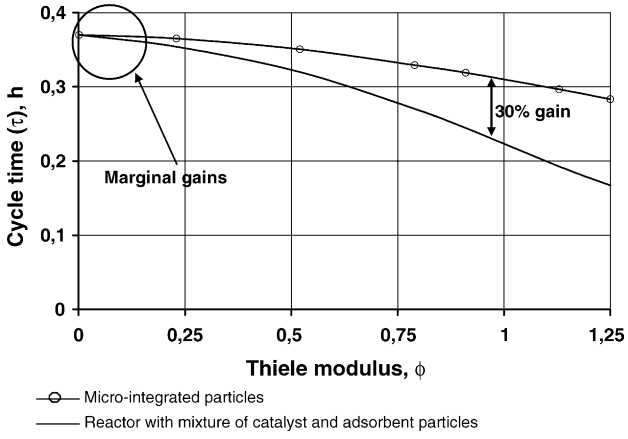

Fig. 7. Influence of transport resistance on process cycle time in Claus process: comparison of performance by conventional adsorptive reactor to micro-integrated adsorptive reactor. Thiele modulus is defined as, $\Phi = l_p\sqrt{r_V(c_0)/D_{eff}c_0}$. It has been defined at reactor entrance conditions.

microstructuring would have had a significant impact on the performance of the adsorptive reactor.

Though the above analysis exposes the shortcomings of concept of microstructuring in an adsorptive reactor, the integration of functionalities at a particle level is still a useful tool to circumvent transport limitations in an adsorptive reactor. Fig. 7 shows the effect of Thiele modulus on the process cycle time for the Claus process. Under low transport limitation conditions, the performance of a micro-integrated particle and functionalities in a separate particle are comparable. With increasing transport limitations, however, integration of functionalities at a particle level reduces the influence of transport limitations in an adsorptive reactor resulting in significantly higher cycle times over conventional adsorptive reactors.

7. Conclusions

In this work, an attempt has been made to understand the influence of distribution of catalyst and adsorbent functionalities at the particle 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 in 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 particle 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 involves a non-uniform distribution of functionalities at the reactor level.

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