Alternative Heterogeneous Contacting Schemes Using Microfibrous Entrapped Catalysts/Sorbents

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Abstract

An innovative contacting system for heterogeneous catalytic reactions and gas adsorption involving Microfibrous Entrapped Catalysts/Sorbent (MECS) has been developed in our lab. These structured catalytic/sorbent systems effectively lower the inter phase and the intra particle fluid-solid diffusion resistances. A MATLAB simulation was performed on a first order reaction system to compare head-to-head performance attributes of a: packed bed, monolith and flow-through pleated microfibrous entrapped catalyst layer. Comparative performance evaluations were modeled at face velocities up to 1200 cm/s. These results show that higher conversion per unit of pressure drop, and higher conversion per unit mass of catalyst, are achieved using MECS systems with pleat factors greater than three. Similar behavior was obtained from experiments supporting the above modeling results.

1. Introduction

Heterogeneous catalytic reactors and gas adsorption systems are used in many chemical and environmental pollution control processes. Currently the various configurations being used for heterogeneous contacting include: packed beds, fluidized beds, trickle bed reactors, structured configurations like monoliths, etc. Some of the major criteria in selecting a particular kind of system for a given application are pressure drop, conversion, selectivity and amount of catalyst or sorbent needed to meet process specifications. The main objective in designing any reaction system is to reduce the pressure drop, increase the conversion and selectivity. All these criteria depend largely on the surface reaction rates as well as the mass, heat and momentum transfer rates inside a catalytic reactor. For a given catalyst loading or kind of adsorbent used the surface reaction or the surface adsorption rates are constant for any type of reactor. But the contacting system remarkably influences the pressure drop, intra-particle and inter-phase heat and mass transfer rates and hence effects the conversion, the selectivity, the amount of catalyst needed and the operating costs of the process.

In an effort to design a system which lowers these inter particle and intra phase transport resistances MECS were developed [1-4]. MECS systems use catalyst/sorbent particles of about 25-200 micron in diameter entrapped within a metal, polymer or ceramic microfibrous matrix consisting mixtures of various ratios of fibers ranging from 2 micron to 50 micron in diameter. A few SEM images of MECS are shown in Fig.1. Production of these patented materials involves standard wet lay paper making techniques and further sintering the dried media at sufficiently high temperatures in hydrogen atmospheres [5],[6]. Also MECS with voidages as high as 98% can be prepared, which can help to reduce the flow-through pressure drop. The micro fiber matrix also acts as a micron scale static mixer eliminating channeling.

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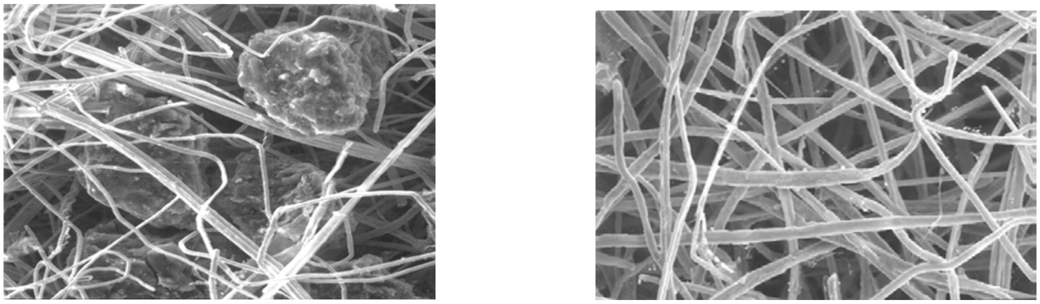

(a) (b)

Fig.1.SEM of sintered composite material of (a) 55–88μm activated carbon and 2, 4 and 8 μm nickel fibers (b) Micro-metal Fiber Matrix of Sintered 2μm Nickel Fibers

2. MATLAB Simulations

MATLAB simulations for a gas phase reaction

$A \rightarrow B$ with $-r_A = k.\, C_A$

in packed beds, monoliths and MECS systems were performed and a systematic comparison is made. First order and isothermal conditions are assumed as very low reactant inlet concentration is considered. The inter-phase mass transfer coefficients and pressure drop for each of the above mentioned reaction systems were calculated using equations shown in the next section. The internal effectiveness factor was obtained from Thiele modulus based formulae. The effective overall rate constant was estimated from above calculations.

The reaction conditions used in simulation:

- Inlet reactants at 400K, 3atm & inlet C_A=1.5 ppmv.
- Surface reaction rate1.35e-5 $m^3/m^2.s$
- Gas viscosity 2.4e-5 kg./m.s and reactant diffusivity 1.15e-5 m^2/s

Comparisons between packed beds of various particle sizes (Voidage=40%), monoliths with various cpsi and MECS of various pleat factors have been made.

3. Equations used in simulations:

3.1. Packed Beds

- Ergun equation for Pressure Drop:

$$\boldsymbol{P} \quad \boldsymbol{v}_0^2 \left(\frac{\boldsymbol{L}}{\boldsymbol{dp}}\right)\times\frac{1}{\mathrm{Re}}\times\left(150+1.75\frac{\mathrm{Re}}{(1-\varepsilon)}\right)\times\frac{(1-\varepsilon)^2}{\varepsilon^3}$$

- Thones Kramers Correlation for External Mass Transfer [7]:

$$Sh' = \mathrm{Re}'^{0.5}\, Sc^{0.33}$$

Where $Sh' = \frac{Sh.\varepsilon}{(1-\varepsilon)} = \frac{kc.dp.\varepsilon}{D.(1-\varepsilon)}$

$$Sc = \frac{\mu}{\rho D}$$

$$\mathrm{Re}' = \frac{\mathrm{Re}}{(1-\varepsilon)} = \frac{\boldsymbol{dp}.\boldsymbol{v}_0.\boldsymbol{\rho}}{\boldsymbol{\mu}.(1-\varepsilon)}$$

3.2. Monoliths [8]

- Pressure Drop Equation:

$$\Delta P = 4f \times \left(\frac{\rho v_{ch}^2}{2}\right) \times \left(\frac{L}{d_{ch}}\right)$$

$f = \frac{13}{\text{Re}}$ For Re<1000

$= \frac{0.03}{\text{Re}^{0.12}}$ For Re>1000

- External Mass Transfer Equation:

$$\boldsymbol{Sh} = 3.655 + 6.874 \times \left(\frac{1000}{\boldsymbol{Gz}}\right)^{-0.488} \times \exp\left(\frac{-57.2}{\boldsymbol{Gz}}\right)$$

Where $\boldsymbol{Gz} = \text{Re}.\boldsymbol{Sc}.\frac{\boldsymbol{d_{ch}}}{\boldsymbol{L}} = \boldsymbol{Graetz}\#$

Re, Sc, Sh Definitions based on d_{ch}

3.3. Microfibrous Entrapped Catalysts / Sorbent (MECS)

- Porous Media Permeability Equation for Pressure Drop [9]:

$$\frac{\Delta P}{T} = 72 \frac{\tau^2}{\cos^2(\theta)} \frac{\mu v_0 (1-\varepsilon)^2}{\varepsilon^3} \left[\left(\sum \frac{x_i}{\phi_i D_i}\right)^2 + x_{FD} \sum \frac{x_i}{(\phi_i D_i)^2}\right] + 6 \frac{\tau^3}{\cos^3(\theta)} \frac{\rho v_0^2}{2} \frac{(1-\varepsilon)}{\varepsilon^3} \left[C_f + C_{FD} \frac{\varepsilon}{4}\right] \sum \frac{x_i}{\phi_i D_i}$$

Viscous losses — Inertial/Kinetic losses

Additional terms: x_{FD} -form drag parameter=e2/12(1-e)
ϕ - Shape factor=3/2 for infinite cylinder
τ - tortuosity =1+(1-e)/2
θ - Angle of flow paths
C_f - Coefficient of friction, 0.174
C_{FD}-Coefficient of form drag=0.6-Cf
x_i - Solid volume fraction of component i
D_i - Size of particle or fiber, cm

- Pfeffer's Theoretical Model for External Mass Transfer for low Re(<70) [10]

$$\boldsymbol{Sh} = \frac{1.25(1-\gamma)^{(1/5)} \boldsymbol{Pe}^{(1/3)}}{\boldsymbol{W}}$$

$$\gamma = (1-\varepsilon)^{(1/3)}$$

$$\boldsymbol{W} = 2 - 3\gamma + 3\gamma^5 - 2\gamma^6$$

$$\boldsymbol{Pe} = \text{Re}.\boldsymbol{Sc}$$

$$\text{Re} = \frac{d_p v_{eff} \rho}{\mu}$$

$$\boldsymbol{v_{eff}} = \frac{\boldsymbol{v}_0}{\boldsymbol{PleatFactor}}$$

Results and analysis:

Fig2. summarizes the results of the above simulations. "Logs of reduction per unit pressure drop" is plotted against velocity for the various systems with above mentioned inlet reactant conditions. Monoliths and MECS show a clear edge over packed beds. This is because the packed beds with larger particles are constrained with intra particle and inter phase mass transfer resistances, where as the smaller particle packed beds are constrained by higher pressure drops.

Also MECS with pleat factors 3 and above show 2-6 fold advantage over monoliths. Pressure drop and conversion predictions favor the usage of MECS. Also MECS exhibited similar higher activity in the many experiments; the results of these experiments are presented elsewhere[12]. Monoliths offer very little resistance to the flow as compared to the other systems as the gas passes through straight channels hence the pressure drop is relatively very low. As such the microfibrous material being made of extremely small diameter fibers offers a lot of resistance to the flow and hence causes high pressure drop. But as the MECS media is quite flexible it can be pleated to obtain lower effective velocities through the media, thereby reducing the pressure drop dramatically.

The internal mass transfer resistance in the monolith catalyst support is reduced as wash coat is generally a thin layer about a 100 μm on the walls of monolith channels. But as the flow in monoliths is mostly laminar and through straight channels, the inter phase (or the external) mass transfer coefficients are extremely low i.e., the external mass transfer resistance is high and hence becomes the rate controlling step. In MECS the flow pattern is mostly controlled my the micron sized fibers so the external boundary layer thickness is small and hence the inter-phase mass transfer resistance is greatly reduced and because the catalyst supports or adsorbent particles used are of order of 100 μm the intra particle mass transfer resistance is also quite low. All this gives the MECS a clear advantage over the other systems.

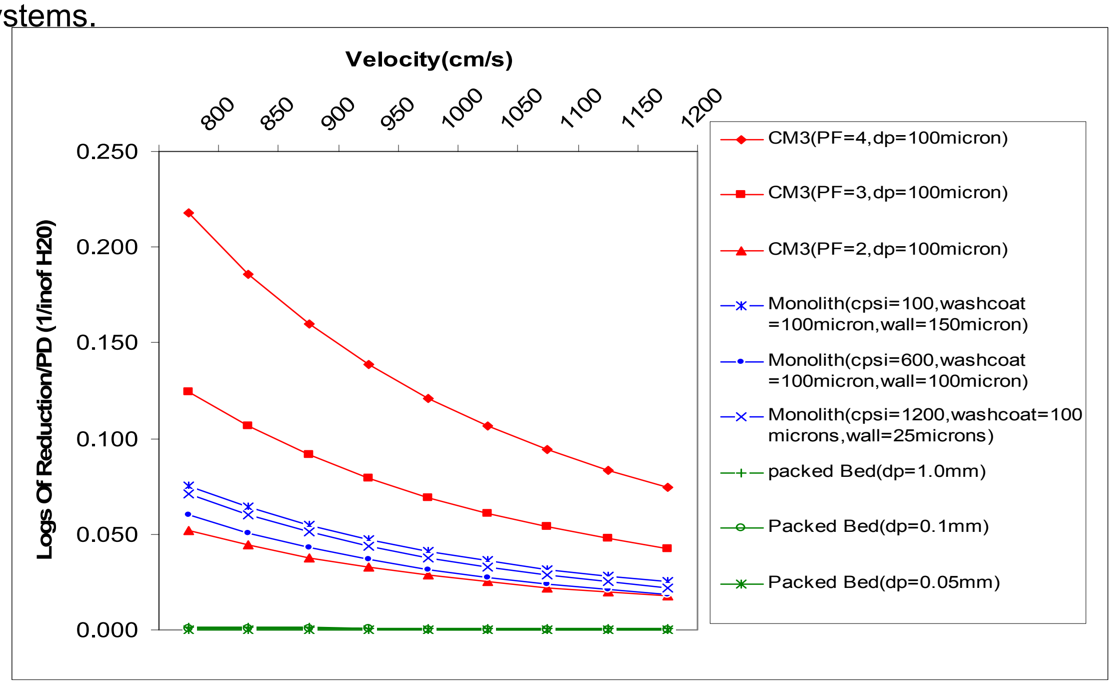

Fig2. MATLAB simulation results of various reactor systems for first order reaction mentioned above.

Conclusions:

- These micro-structured material with low mass transfer resistances as they exhibit 2-6 times higher activity they make a better utilization of the noble metals and other catalysts and adsorbents. This can help bring down the capital costs on catalysts to as low as 30% of the existent systems in some cases.
- Lower pressure drop means lower operating costs.
- Operating costs can also be reduced by operating the systems at lower temperatures and pressures as compared to other systems.
- Polishing filter concept in which a packed bed or monolith is used before the MECS appears really rewarding.
- Further analysis on exothermic, endothermic reactions and reactions involving high selectivity need to be investigated.

Nomenclature:

C_D = coefficient of drag for sphere in turbulent flow
C_f = coefficient of friction for turbulent flow
C_{FD} = coefficient of form drag of sphere in turbulent flow (CFD = CD − Cf)
d_p = diameter of characteristic size of any arbitrary shape (m)
d_{ch} = Monolith channel diameter
f = Friction factor in monolith
Gz=Graetz number
L = Length of reactor normal to the flow
ΔP = Pressure drop across fixed bed
Re = Reynolds number
Sc = Schmidt number
Sh = Sherwood Number
v_0 = Face velocity (cm/s)
V_{ch} = Velocity inside the monolith channel
x_{FD} = Form drag parameter, x_{FD} = ε2/12(1 − ε)
x_i = Volume fractions of components in bed of solids

Greek symbols
ε = Void fraction of bed
θ = Angle of flow paths through bed (◦)
μ = Fluid viscosity (P) or (g/cm s)
ρ = Fluid density (gm/cm3)
τ = Tortuosity of cubic cell with one sphere
φ = shape factor for any arbitrary shape, φ = 6/Dav

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