

Catalysts

- Speed up the reaction → Cost saving for industrial processes
- Lower activation energy

Fundamental properties req. to a catalyst,

- Activity → Selectivity → stability → Morphology
- Mechanical strength → Thermal properties → cost
- Regenerability → Originality

High activity of a catalyst is defined as high productivity from a smaller reactor or milder reaction conditions

High selectivity of a catalyst is defined as high yield of desired product, suppression of undesired reactions, reduction of internal diff. to mass diff.

Good catalytic stability is stability changing very slowly with the course of reaction and regeneration

- Causes for change in activity, selectivity and stability of a catalyst.
 - Coke forms on catalysts in diff. m's
 - Reactants, pdts or poisons may attack active agents
 - Crystals of deposited metal may become enlarged.
 - Change in crystalline structure of support can cause a loss of mechanical strength.
 - Progressive adsorption of trace poisons in feed.
- External morphological characteristics of a catalyst must be suited to the process, (for spherical form
 - (For moving bed, spherical form is preferable,
For fluidised bed, spherical powder is pref.)
- Ascending order of relative AP in reactor for diff. catalyst forms
 - Rings < Beads < Pellets < Extrudates < Crushed
- Mechanical strength is defined as the resistance to crushing, resistance to wearing out of a particle from solid surface by touching of another), resistance to wearing out by friction, resistance to wearing by contact with fluids
- A catalyst should have high thermal conductivity and specific heat as reduced temp. gradient within grains as well as catalyst bed and improved heat transfer for exothermic and endothermic rxn.

- Regenerability is regeneration of catalyst when it is insuff for the process due to aging of the catalyst.
- Originality, catalysts and process should be licensed (patents)
- Cost, catalysts must be cheap compared to comp. catalysts.

Catalyst Development steps

Discovery → Prep → Testing → Manufacturing

Regeneration ← Steady state ← Activation

Operation

- Catalyst is a chemical process charac. by its composition and method of prep. Operations used are precipitation, impregnation, ripening, filtration, washing, drying, calcination and activation
- Bulk catalysts comprise of active substances. It depends on strength req. under m' cond. and reactor type.
- Supported catalysts are prepared for obtaining bifn. catalyst, high dispersion of active phase, better diffusion of gases through the bed, better mech. design

to attrition, better thermal conductivity.

Catalyst Supporters

- Avg. pore size and pore size distn: should be such that the physical limitations aren't placed on conversion.
- May have low/high surface area
- Low surface area supports are used when high activity per unit mass is less imp.
- Low surface area are considered when cost is one of the major factors

Promoters

- Imparts improved charac. to the catalysts.
- The promoter may change the electronic structure of solid in such a way that the activity per unit area is increased.
- They may catalyze an int. step.
- They may slow down or influence crystal formation and growth or produce lattice defects; which may lead to higher activity per unit area

Inhibitors

- they are a type of promoters who may influence the selectivity by poisioning undesired rxns.

Stabilizers

- Inhibits the loss of active surface area during operation; inhibits sintering of active sites and growth of micro crystalline regions.

Surface characterization

- To be effective, catalyst should have surface area in the range of $5-1000 \text{ m}^2/\text{g}$
- For highly porous catalysts the global rate of reaction is dependent on geometrical poros. of catalyst pores. Rate of adsorption of gas is dependent on internal pore surface. More the rate of adsorption, more will be the rate of chemical rxn.

To determine the surface area of a catalyst N_2 is poured at -195.8°C (B.P) over a range of pressure below 1 atm, the amount of N_2 adsorbed is the surface area. The data obtained are a series of gas vol. at diff. pressure and at a particular temp. Volumes are corrected to cm^3 at 0°C and 1 atm (STP). Plot is made by vol. against pressure to v.p. This is called the classical BET Method (Brunauer- Emmet and Teller method)

BET Flow Method

Mixture of non-adsorbable gas (He) and adsorbable gas (N_2) is passed over the solid. The partial pressure of the adsorbable gas is varied keeping P_T const.

The adsorption is done till equilibrium is reached. The adsorbed gas is desorbed by heating and is collected by passing He on it. The volume desorbed is measured by a thermal conductivity cell. This process volume give a single point on the isotherm. It is repeated for various partial pressures thereby forming the isotherm.

Langmuir Isotherm

For monolayer Adsorption

$$\frac{K_p}{1 + K_p} = \frac{v}{v_m}$$

$$\frac{P}{v} = \frac{1}{v_m} + \frac{P}{v_m}$$

$\kappa = \frac{k}{k'}$ = Adsorption eq. constant

$v = \kappa'$ volume of gas adsorbed at any time

v_m = monomolecular layer vol.

P = Pressure of gas

BET eqn. for multilayer adsorption

$$\frac{P}{v(P_0 - P)} = \frac{1}{v_m c} + \frac{(c-1)P}{c v_m P_0}$$

P_0 is saturation or vapour pressure and c is const. for particular temp and gas-solid system

BET plot, $\frac{P}{v(P_0 - P)}$ vs $\frac{P}{P_0}$ is a st. line

Intercept, $I = 1/v_m c$ Slope, $S = c-1/v_m c$

$$\therefore v_m = 1/I + S$$

Monomolecular layer vol. can be converted to no. of molecules adsorbed

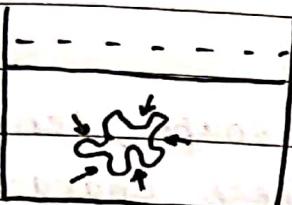
$$s_g = \left[\frac{v_m \text{ No}}{v} \right] \alpha \quad \begin{matrix} \text{Area covered} \\ \text{by one adsorbed} \\ \text{molecule.} \end{matrix}$$

$$\alpha = 1.09 \left[\frac{M}{N_A P} \right]^{2/3}$$

↳ vol. of one adsorbed molecule

Void volume and solid density

He - Hg method of determination of void vol., the volume of He displaced by a sample of catalyst is measured. Then the He is removed and the vol. of mercury that is displaced is measured. The vol. of He displaced is a measure of vol. occupied by the solid material. From this and weight of sample, the density of solid phase ρ_s can be obtained.



\Rightarrow He disp.
volume

He enters into the pores leaving
the solid part of pellet.
Hence, He displaces the ^{solid} _{total} vol.

while Hg displaces the total volume

Porosity (ϵ_p) = Void vol. of particle / Total vol. of particle

$$\epsilon_p = \frac{V_g \rho_s}{V_g \rho_s + 1}$$

$m_p \rightarrow$ mass of the particle $V_g \rightarrow$ Void vol. per gram

Sample mass collected by Hg vol. gives the density ρ_p of porous particles

$$\epsilon_p = \rho_p V_g$$

Pore System

Monodisperse Pore System : catalyst particle containing single type of void region (micropore)

Bidisperse Pore System : catalyst pellet containing two void regions (micro and macropore)
↳ within the particle ↳ between the particles

Pore Volume Distribution

Pores are non-uniform in size, shape, length are interconnected to each other. These characteristics change from catalyst to catalyst. It is assumed that pores are cylindrical with radius 'a'

Pore sizes in catalyst range from $10-10,000 \text{ \AA}$ and Hg has is preferred liq to measure these as it has significant surface tension which prevents it from entering most of the pores. For ranges about $100-200 \text{ \AA}$ a simple Hg - porosimeter is used, but high pressure apparatus is req. to find the pore vol. below 200 \AA by Hg. At this range we use N_2 - adsorption desorption method

N_2 adsorption - desorption method

- Similar to surface area determination
- N_2 adsorption is continued until N_2 pressure approached the saturation pressure
- At $P/P_0 \rightarrow 1$, all pores are filled with adsorbed and condensed N_2

→ Desorbed N_2 at each increment is measured. r.p. of a liq. evaporating from a capillary $\propto r$ of capillary. Hence, volume desorbed is plotted against pore radius.

A combination of Hg penetration and N_2 adsorption desorption method covers the determining of pore volume of a bidisperse catalyst. For mono disperse catalyst, only N_2 adsorption-desorption process is suff.

Hg - penetration process $\pi a^2 p = -2\pi a \sigma \cos \theta$

$$a = \frac{-2\sigma \cos \theta}{p}$$

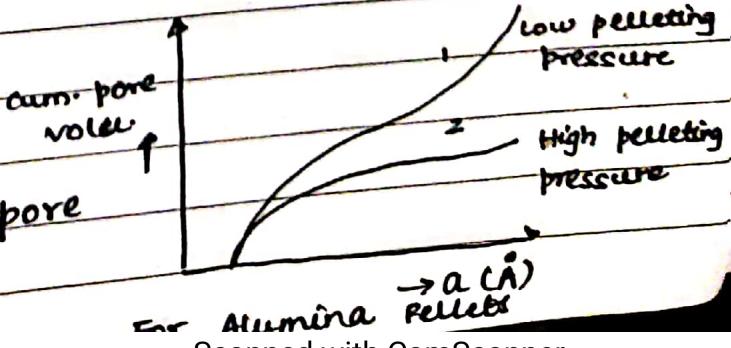
$a \rightarrow$ pore radius in Å, $\sigma \rightarrow$ surface tension of Hg

$P \rightarrow$ applied pressure (psi) $\theta \rightarrow$ contact angle.

$$\theta \approx 140^\circ, a(8) = 8.75 \times 10^5 / P(\text{psi})$$

- Plot of cumulative pore vol. against pore radius is penetration curve
- Penetration vol. at any pore radius a is the vol. of pore just larger than a (?)
- $\Delta V/\Delta a$ is the vol. of pores between a and $(a+\Delta a)/\Delta a$
- Plot of pore radius on logarithmic scale and the derivative of distn' fn., $dV/d(\log a)$ gives distn' curve. This curve shows rate of change of pore vol. with change in pore radius.

Increasing pelletting pressure, drastically reduces the macropore volume.



Parallel pore Model

Avg. pore radius (\bar{a}) is assumed. All pores are considered to be st. cylindrical, they have same pore radius \bar{a} , same length \bar{l} . This model is called Wheeler Parallel Pore Model

$$m_p s_g = (2\pi \bar{a} \bar{l}) n$$

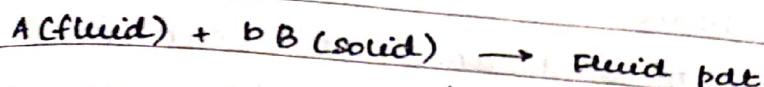
$$m_p v_g = (\pi \bar{a}^2 \bar{l}) n$$

m_p and n are mass and number of pores per particle

$$\text{The avg. pore radius, } \bar{a} = \frac{2V_g}{s_g}$$

This model agrees well with monodisperse catalyst

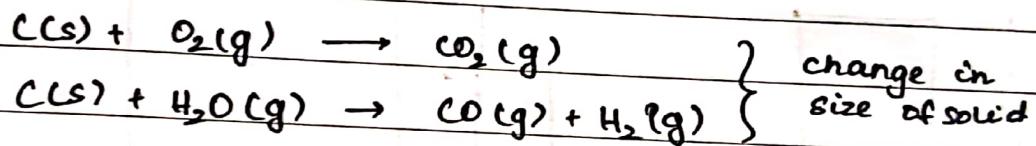
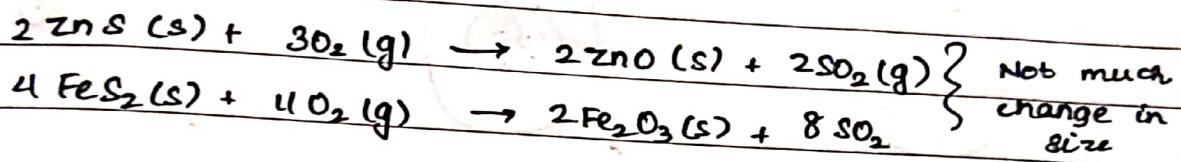
Fluid - Solid Particle Reactions



↓
Solid pdt

↓
Fluid & solid pdt

Solid particles remain unchanged in size during rn: when the pdt. they form are firm and non-flaking ash material. The particles shrink in size during rn: when a flaking ash or pdt. material is formed.

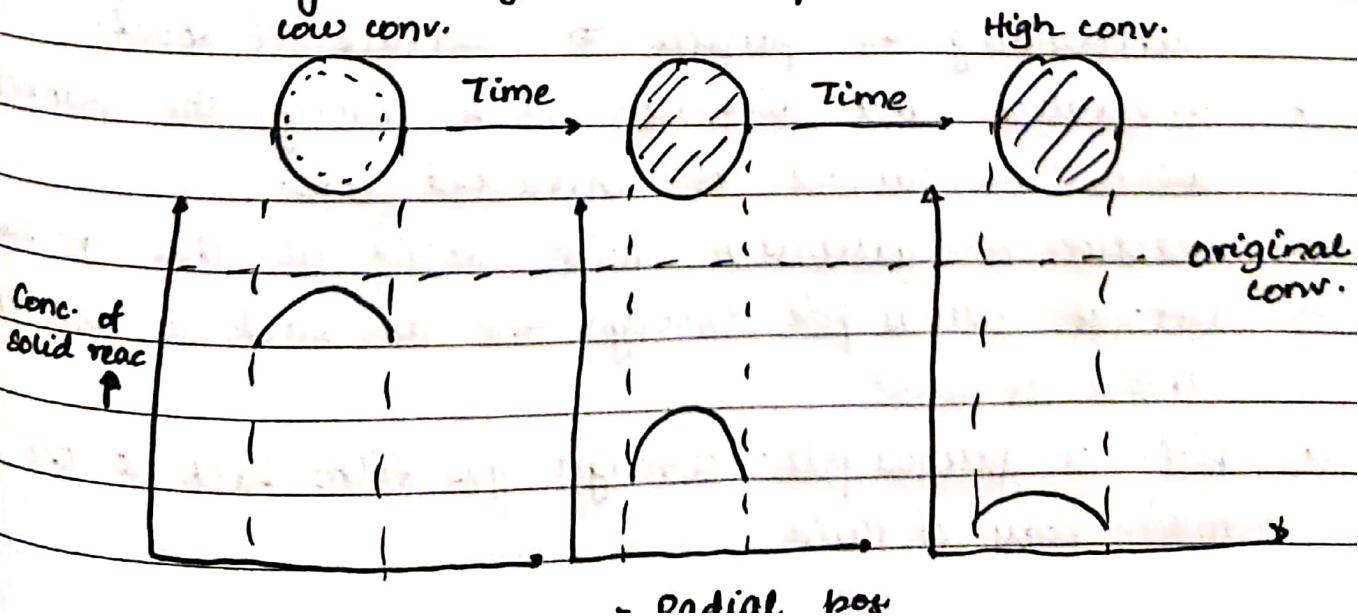


For non-catalytic rn's of particles with surrounding fluids, two simple idealized models are considered

a) Progressive Conversion Model

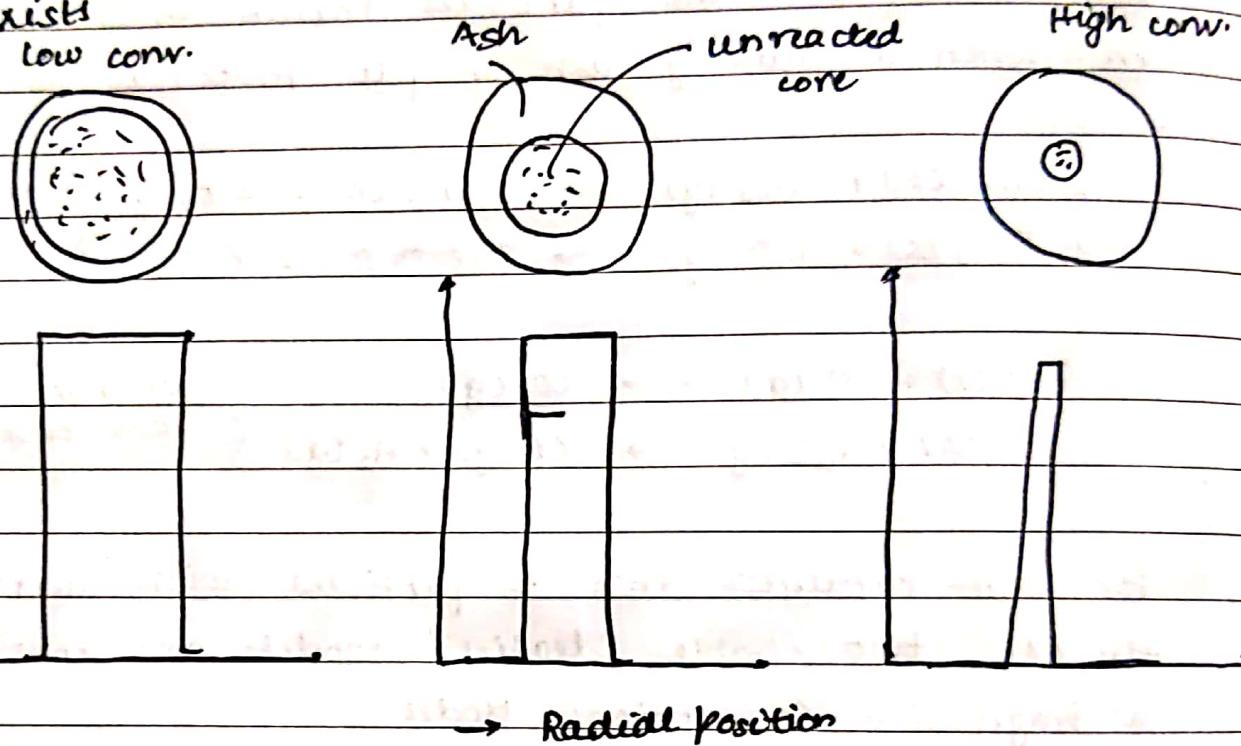
It is assumed that the reactant gas enters and reacts throughout the particle at all times, most likely at diff rates at diff. locations within the particle.

Thus the solid reactant is converted cont. and progressively throughout the particle



Shrinking Core Model

In this model, m' is assumed to occur first on the outer skin of the model particle. The zone of m' then moves into the solid, leaving behind completely converted material and inert solid, which are referred to as "ash". Thus at any time there exists



SCM approximates real particles more closely than does the PCM

- (S1) → Diffusion of gaseous reactant A through the film surrounding the particle to surface of solid.
- (S2) → Penetration and diffusion of A through the blanket & ash to the surface of unreacted core.
- (S3) → Reaction of gaseous A with solid at this m' surface
- (S4) → Diff. of gaseous prod. through the ash back to the exterior surface of solid
- (S5) → Diff. of gaseous prod. through gas film back to the main body of fluid

Diffusion through gas film controls

Whenever the resistance of the gas film controls, the conc. profile for gaseous reactant A

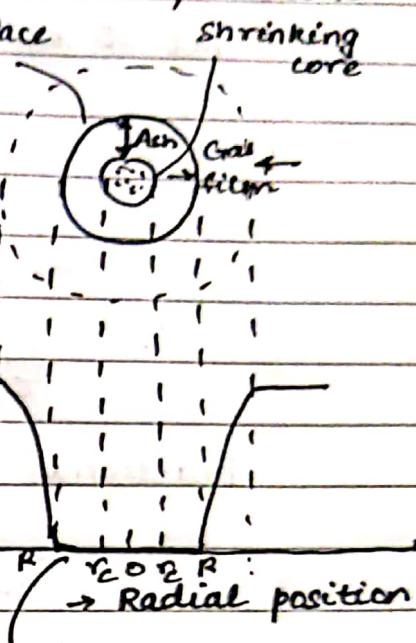
For the m' ,



So, unchanging exterior surface

$$dN_B = b dN_A$$

$$C_{A,\infty} = C_{A,C}$$



$$\frac{-1}{\text{Surf}} \frac{dN_B}{dt} = \frac{-1}{4\pi R^2} \frac{dN_B}{dt}$$

For inner m'

$$C_{A,C} = 0$$

$$= -\frac{b}{4\pi R^2} \frac{dN_A}{dt} = b k_g (C_{A,g} - C_{A,C}) = b k_g C_{A,g} = \text{const}$$

ρ_B is molar density of B in the solid

v is volume of particle

$$N_B = \rho_B v$$

The decrease in v_C or radius of unreacted core accompanying disapp. of dN_B moles of solid reactants,

$$-dN_B = -b dN_A = -\rho_B dv = -\rho_B d\left(\frac{4}{3}\pi r_c^3\right) = 4\pi \rho_B r_c^2 dr$$

$$-\frac{1}{\text{Surf}} \frac{dN_B}{dt} = -\frac{\rho_B r_c^2}{R^2} \frac{dr_c}{dt} = b k_g C_{A,g}$$

Mass transfer
w/o fluid
and particle

$$t = \frac{P_B R}{3b k g C_{Ag}} \left[1 - \left(\frac{r_c}{R} \right)^3 \right]$$

Let τ be the completion time, i.e. $r_c = 0$

$$\tau = \frac{P_B R}{3b k g C_{Ag}}$$

$$\therefore \frac{t}{\tau} = 1 - \left(\frac{r_c}{R} \right)^3$$

Fractional conversion (x_B),

$$1 - x_B = \left(\frac{r_c}{R} \right)^3 \Rightarrow \frac{t}{\tau} = x_B$$

Diffusion through ash layer controls

Q_{AS} → Flux of A through exterior surface of particle (Inward +, Outward -)

Q_A → Flux of A through surface of any radius r

Q_{AC} → Flux of A through m. surface

Considering partially reacted particle, both reactant^A and boundary of unreacted core move inward toward center of particle. But for gas/solid systems, the shrinkage is slower than flow rate of A toward the unreacted core of about 10^3 . Thus, it is reasonable to consider that the conc. gradient of A in the ash layer at any time is const. This isn't the case for G/s system.

For G/S system, we use the steady state assumption.
Rate of ṁ of A at any instant is given by,

$$-\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{AS} = 4\pi r_c^2 Q_{AC} = \text{const.}$$

For equimolar counter diffusion, Fick's law,

$$Q_A = D_e \frac{dc_A}{dr}$$

Effective diffusivity
of gaseous reactant
in air layer

$$-\frac{dN_A}{dt} = 4\pi r^2 D_e \frac{dc_A}{dr} = \text{const.}$$

Integrating from R to r_c

$$-\frac{dN_A}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = 4\pi D_e c_{Ag}$$

const.

Eliminating N_A ,

$$t = \frac{P_B R^2}{6b D_e c_{Ag}} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right]$$

For complete conversion, $\tau = \frac{P_B R^2}{6b D_e c_{Ag}}$

$$\frac{t}{\tau} = \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right]$$

$$= 1 - 3(1-x_B)^{4/3} + 2(1-x_B)$$

Chemical Rn' Controls

Since, the progress of the rn' is unaffected by the presence of any ash layer, rate is prop. to available surface of unreacted core.

$$-\frac{1}{4\pi r_c^2} \frac{dN_A}{dt} = -\frac{b}{4\pi r_c^2} \frac{dN_B}{dt} = b k'' C_{Ag}$$

↳ First order
rate const. *
surface m.

On solving, $t = \frac{P_B}{b k'' C_{Ag}} (R - r_c)$

For complete conversion, $\tau = \frac{P_B R}{b k'' C_{Ag}}$

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - x_B)^{1/3}$$

Rate of rn' for shrinking particles

- (21) → Diffusion of A from main body of gas through the gas film to surface of solid
- (22) → Rn' on surface b/w A and solid
- (23) → Diffusion of the reaction prod. from the surface of the solid through the gas film back into the main body of the gas.

Chemical Rn' controls : When the chemical rn' controls the behaviour is identical to that of the particle of unchanging size.

Gas Film Diffusion Controls

Film resistance at the surface of particle is dependent on numerous factors, such as rel. vel.

Froessling correlation,

$$k_g \frac{dp}{dy} = 2 + 0.6 \left(\frac{u}{ED} \right)^{1/3} \left(\frac{dp \cdot u_p}{y} \right)^{1/2}$$

During m: particle size changes, hence k_g varies.

For small dp and u , $k_g \sim \frac{1}{dp}$

For large dp and u , $k_g \sim \frac{u^{1/2}}{dp^{1/2}}$

Stokes Regime (Considered for small particles)

$$dN_B = P_B dV = 4\pi P_B R^2 dR$$

$$-\frac{1}{S_{eq}} \frac{dN_B}{dt} = \frac{P_B 4\pi R^2}{4\pi R^2} \frac{dR}{dt} = -P_B \frac{dR}{dt} = b k_g C_{ag}$$

$$\text{At Stokes Regime, } Sh = 2 \Rightarrow k_g = \frac{2D}{dp} = \frac{D}{R}$$

$$\therefore t = \frac{P_B R_0^2}{2b C_{ag} D} \left[1 - \left(\frac{R}{R_0} \right)^2 \right]$$

$\hookrightarrow \tau$

$$\frac{t}{\tau} = 1 - \left(\frac{R}{R_0} \right)^2 = 1 - (1 - x_B)^{2/3}$$

Combination of Resistances

Time to reach any stage of conversion

$$t_{\text{total}} = t_{\text{film alone}} + t_{\text{ash}} + t_{\text{m. alone}}$$

$$T_{\text{total}} = T_{\text{film}} + T_{\text{ash}} + T_{\text{m.}}$$

$$\frac{-1}{S_a} \frac{dn_B}{dt} = \frac{bC_A}{\frac{L}{k_g} + \frac{R(R-r_c)}{r_c D_e} + \frac{R^2}{k'' r_c^2}}$$

film ash m.

Limitations of Shrinking Core Model

- Assumption may not match reality. The m. may occur under diffuse front rather than a sharp interface
- For fast m., rate of heat release may be high enough to cause significant temp. gradient

AMAZING FACTS

The sun and moon appear to be the same size in the sky because of an astonishing coincidence—the moon is 400 times smaller, but 400 times closer.

The Glass-winged butterfly lacks coloured scales, which makes its wings transparent and helps it avoid predators.

Similar to Scotland, North Korea also has a mythical animal as its national emblem—the winged horse Chollima.

A solar-powered, 'self-filling' water bottle has been invented for bike riders. It condenses atmospheric moisture to automatically fill the bottle with safe drinking water.

There are about 60,000 miles of blood vessels in a child's body. If you took them all out, and laid them end to end, they would wrap around the world more than twice.

