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Pseudo-steady state method on study of xylose hydrogenation in a trickle-bed reactor

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Abstract

A new approach to assess the overall mass transfer coefficients in a partial wetting trickle-bed reactor was proposed and tested in hydrogenation of xylose. An effective data-acquiring procedure featured by recycling a large volume of liquid feed has been adopted after the steady state operation. Since the volume of the fresh feed taken for recycling was so large that the xylose feed concentration decreased slowly during the prolonged recycling period, the pseudo-steady state was therefore achieved. By relating outlet and inlet xylose contents in liquid flow of the reactor, the reaction results varied with xylose feed concentration were simulated. The coefficients of the two reactants, hydrogen and xylose, were correlated simultaneously with a steady state reaction model. The estimated coefficients fell in the range of trickle-bed reactors at low flow rates and manifested a partial wetting status.

Keywords: Mass transfer coefficients; Pseudo-steady state; Trickle-bed reactor

1. Introduction

Trickle-bed reactor is usually operated at low gas and liquid flow rates, in which wetting of catalyst particles can be incomplete normally when the liquid superficial velocity is less than 3 mm/s. The effect of partial wetting on the local reaction rate proved significant and complex, especially for reactions in which the limiting reactant is present in the gas phase [1].

As in the case of xylose hydrogenation to xylitol ($C_5H_{10}O_5+H_2\rightarrow C_5H_{12}O_5$), hydrogen solved in solution at 0.8 MPa is two magnitudes more dilute than xylose in feed (1.0 kmol/m^3), while its diffusivity is only five times larger, therefore it is a typically hydrogen deficit reaction. It is calculated at above conditions that the conversion of xylose could be three times higher when wetting efficiency is 0.75 than complete wetting, due to the much easier access of hydrogen through the ''dry'' particle surface [2].

The depiction of wetting status and its effect on reaction has inspired years of interests [1]. But due to the high complexity of the problem, it is still far from successful [3].

Turek et al. [4] proposed a direct way in dealing with the partial wetting effect by lumping it into the overall mass transfer coefficients. They established a complete wetting model and the overall mass transfer coefficients are correlated from partially wetted trickle-bed reactors [4]. As this model depicts well their experimental results, in hydrogenation of glucose to sorbit, the same approach is adopted in our study.

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In this paper, we focus on developing an effective and reliable method to determine the lumped overall mass transfer coefficients in a partial wetting trickle-bed reactor.

2. Experimental

As mass transfer coefficients are rather independent of xylose concentration, other properties remain the same, while the reaction rate does concern with xylose concentration. It is therefore reasonable to correlate the overall transfer coefficients from the reaction results at differed xylose feed concentration and otherwise identical conditions.

But this approach meets with some difficulties in practice. First, it is time consuming and costly to change the feed concentrations by steps and sampling after each steady state establishes. Also, the properties of the solution-like density and viscosity will change with xylose feed concentration, leading to differed wetting status and mass transfer rates. To repress this effect, xylitol should be added to make the sum of xylose and xylitol in feed constant. To avoid these difficulties, the pseudo-steady state procedure was developed as given below.

Shown in Fig. 1 is the schematic diagram of the experimental apparatus. It is composed mainly of two columns, preheater column 6 and reactor column 7. Gas and liquid are fed into 6 and heated to a temperature of 5°C below that of reaction. The retained liquid in 6 is about 800 ml and fresh feed at point A is 15–35 ml/min. To provide an adequate contact time for liquid and gas feed to saturate each other before reaction, most of the outlet liquid from 6 is refluxed from point C to B with pump 5 at 110 ml/min.

There are three successive sections of packing layers in 7, the first and last are inert layers of glass beads for flow distribution, the second is packed with 6 ml shell activated Raney-Ni particles. The feeds are heated further to the reaction temperature in the first packing section.

The pseudo-steady state procedure starts the same way as steady state operation, i.e. set the input xylose

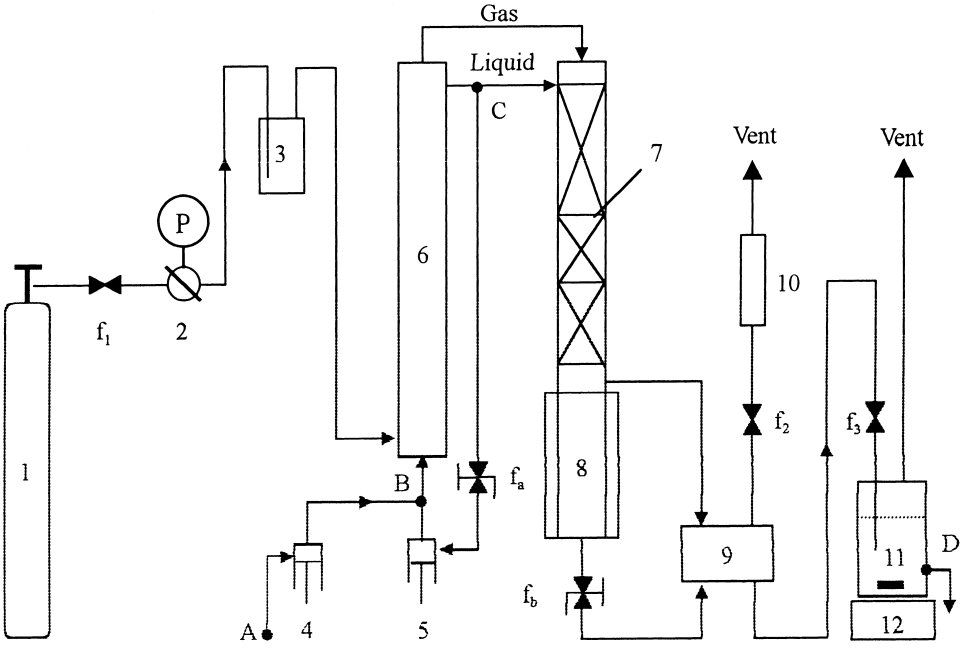

Fig. 1. Schematic diagram of the experimental apparatus: 1, Hydrogen cylinder, 2, Pressure regulating valve, 3, Humidifier, 4, 5, Liquid pump, 6, Preheater column, 7, Reactor column, 8, Water cooler, 9, Gas-liquid separation tank, 10, Gas flow meter, 11, Liquid reservoir, 12, Magnetic stirrer, f_1–f_3, Needle valves, f_a, f_b, Sampling valves, P, Precision bar meter, A–D, Operation points.

concentration C_{x0} constant, and keep the gas and liquid flow rate steady. The steady state established after the temperature is constant and the outlet xylose concentration C_{xb} (sampled at valve f_b) approaches a steady value.

Next, refill the liquid reservoir 11 with 600 ml fresh xylose feed (concentration C_{x0}), mix it continuously with the outflow of 9 by stirrer 12, and feed the mixed liquid from point D to A with pump 4. The total amount of recycled liquid feed is about 1400 ml, i.e. 600 ml in reservoir 11 and about 800 ml inside column 6, 40–100 times the rate of fresh liquid feed per minute. Take x as per pass conversion, the xylose input concentration C_{xa} (sampled at valve f_a) changes continuously at the speed of about 0.025–$0.01xC_{x0}\ \mathrm{min}^{-1}$, and this value in our system is always kept below $0.0038C_{x0}\ \mathrm{min}^{-1}$. So it is reasonable to treat the prolonged recycling period as pseudo-steady state.

By sampling C_{xa} at f_a and C_{xb} at f_b, and relating them with the average residence time t_r, a series of reaction results, i.e. $C_{xa}(t)$ at inlet and $C_{xb}(t+t_r)$ at outlet, can be obtained. The parameter t_r for each run is calculated by dividing the dynamic liquid hold-ups in 7 and 8 by liquid flow rate.

3. Reactor model

As discussed above, the pseudo-steady state and partial wetting process can be simulated with a steady and complete wetting model, as presented below:

3.1. Reaction kinetics

It is measured in an autoclave with fine Raney-Ni powder, the average diameter 14 μm [5]. Only the result is presented here:

$$r_v = \frac{k_v K_H C_H}{1 + K_H C_H} C_x,$$
$$k_v = 6.362 \times 10^7 \exp(-7012/T)\ \mathrm{m^3/(m^3\text{-}cat\ s)},$$
$$K_H = 2.623 \times 10^2 \exp(-484/T)\ \mathrm{m^3/kmol}. \quad (1)$$

In a batch tank reactor, the activities of the particle catalyst were tested, and found that the intrinsic parameter k_v may decrease by a factor of 2–5. Since the micro-conditions in the activation of particle and powder Raney-Ni cannot be the same, and the ratio of activities may also change at different reaction conditions, $a_r=(k_v)_{particle}/(k_v)_{power}$ is therefore induced.

3.2. Effectiveness factor (η_s)

η_s is the effectiveness factor, and subscript s denotes the properties at the particle surface. The catalyst particles are irregular and the shell-activated, the porously activated layer depth of 110–130 μm was measured with a microscope photographer. It is simplified as a flat plate with featured length $L=V_p/S_p$, the upper 0–δ_L corresponds to the active layer, and reactants transport only through the top surface.

Robert and Satterfield [6] inferred the effectiveness factor for a Langmuir–Hinshelwood style reaction of a one-reactant system, and it is extended here to a two-reactant system:

$$\eta_s=\sqrt{2}\Phi^{-1}\frac{1+y}{1+E}\left[\frac{1-h}{2}+(E-y)\left(1-h-y\ln\frac{y+1}{y+h}\right)\right]^{1/2}, \quad (2)$$

where $\Phi=L[(a_r k_v)/(\epsilon_p D_x/\tau)]^{1/2}$, $y=1/(K_H C_{Hs})$, $E=D_x C_{xs}/(D_H C_{Hs})$, $h=C_{HL}/C_{Hs}$. C_{xs} and C_{Hs} are the concentrations of xylose and hydrogen at the particle surface, respectively. ϵ_p is the porosity of the activated layer, and τ is the torture factor. D_x and D_H are diffusivities of xylose and hydrogen in solution, respectively. C_{HL} is the hydrogen concentration at position δ_L, which is zero in this system, since hydrogen is always depleted before it arrives at the boundary.

3.3. Mass balance in bulk flow

It is assumed that plug flow in gas and liquid phase, no axial dispersion, no pressure drop, isothermal, and constant mass transfer coefficients along the bed. The differential equation for xylose concentration C_{xz} is expressed as

$$u_L\frac{dC_{xz}}{dz} = -(1-\epsilon_b)\eta_s r_v(C_{xs}, C_{Hs}),$$
$$\text{B.C.}: z = 0,\ C_{xz} = C_{xa}(t), \quad (3)$$

where u_L is the superficial liquid velocity, z the bed length, and ϵ_b is the void volume of the bed. Since the rate of mass transfer equals the rate of reaction at

steady state, therefore

$$K_G a_p(\alpha_H P_H - C_{Hs}) = \eta_s r_v(C_{xs}, C_{Hs}) \quad \text{for hydrogen} \tag{4}$$

and

$$K_L a_p(C_{xz} - C_{xs}) = \eta_s r_v(C_{xs}, C_{Hs}) \quad \text{for xylose.} \tag{5}$$

The initial value of K_G and K_L are guessed to iterate C_{xs} and C_{Hs}, then integrate Eq. (3) to calculate C_{xz} at the bed outlet. K_G and K_L are optimized by comparing the calculated C_{xz} with $C_{xb}(t+t_r)$.

4. Results and discussion

Six runs of pseudo-steady state operation, numbered as 1–6, are taken. Bed i.d. is 21 mm and dumping volume ~6 ml. The particle diameter d_p, featured length L, activated layer depth δ_L and main operation conditions are listed. The superficial liquid velocity u_L, which decide largely the extent of wetting status of the bed and hence the overall mass transfer rates, is changed from 0.73–1.70 mm/s. While the gas velocity, found to be of little effect, is kept constant at 1.55 mm/s under reaction conditions.

Depicted in Fig. 2 are the typical C_{xa} and C_{xb} for bed 1 and 2, the curves are smooth and the C_{xa} and C_{xb} decrease slowly with time as expected. With the residual time t_r measured, each $C_{xa}(t)$ can be coupled with a $C_{xb}(t+t_r)$. As the beds are mainly packed by inert particles of one size, t_r are necessarily identical for different catalyst sizes when liquid velocity is the same as shown in Table 1.

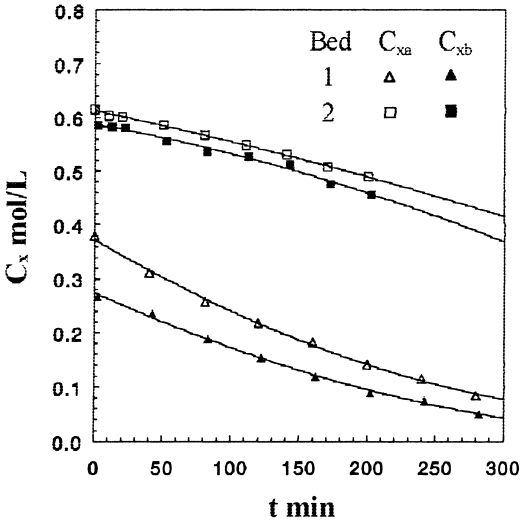

Fig. 2. C_{xa} and C_{xb} measured in bed 1 and 2.

The overall mass transfer coefficients $K_G a_p$ and $K_L a_p$ and the parameter $a_r \epsilon_p/\tau$ are correlated by a nonlinear least square method with 20–30 pairs of $C_{xa}(t_i) \sim C_{xb}(t_i+t_r)$ for each run. The correlated values are given in Table 1, from which we can see that $K_G a_p$ and $K_L a_p$ fall in the range of mass transfer coefficients measured in low Reynolds number trickle-bed [7,8], while $(a_r \epsilon_p/\tau)$ fall mainly within 0.02–0.04. If the

Table 1
The reaction conditions (u_G=1.55 mm/s) and correlated model parameters

	Bed					
	1	2	3	4	5	6
d_p (mm)	0.45–0.67	0.45–0.67	0.74–0.85	1.0–1.2	1.0–1.2	1.0–1.2
L (mm)	0.0822	0.0822	0.134	0.195	0.195	0.195
δ (mm)	0.0701	0.0701	0.0855	0.0938	0.0938	0.0938
u_L (mm/s)	1.2	1.45	1.45	0.73	1.7	1.7
T (K)	383	383	383	383	383	393
P_H (MPa)	4	2	4	4	4	4
t_r (min)	7.0	6.5	6.5	11.0	5.0	5.0
$a_r \epsilon_p/\tau$	0.022	0.019	0.035	0.026	0.026	0.056
$K_L a_p$ (l/s)	0.276	0.321	0.15	0.204	0.306	0.360
$K_G a_p$ (l/s)	0.479	0.258	0.505	0.470	0.447	0.289

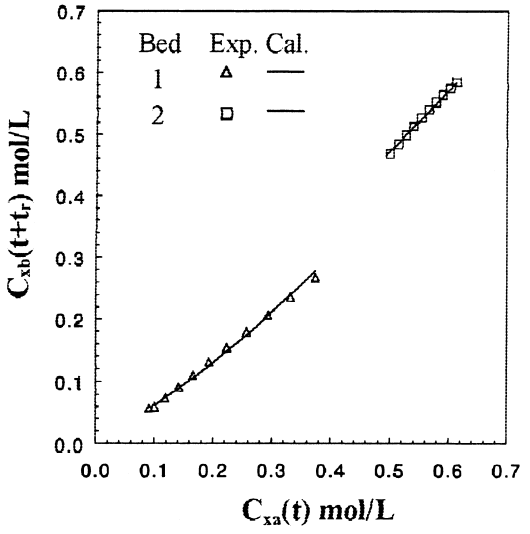

Fig. 3. Simulation results for bed 1 and 2.

value of ϵ_p/τ is assumed 10, the a_r is about 0.2–0.4, near the value of 0.2 in [4], where the particle Raney-Ni catalyst was also used.

The discrepancies between the model and experiment are little in all the beds. To save the space, only the results for bed 1 and 2 are illustrated in Fig. 3. The outlet concentrations change almost linearly with the feed concentrations, show a pseudo-first order kinetics with xylose concentration. The slope of curves alter obviously if any of the parameters in model is changed by 10%. In both bed 1 and 2 and bed 4 and 5, $K_G a_p$ decrease with u_L, while $K_L a_p$ increase at the same time.

Since in this gas phase limited reaction, η_s increases with $K_G a_p$, that is, with the liquid velocity is reduced. This phenomenon cannot be explained by complete wetting mechanism and thus manifest a partial wetting status of the bed.

5. Conclusion

Measuring the overall mass transfer coefficients of more than one reactant at a time is seldom tackled before, especially in modeling of a partially wetted trickle-bed reactor. The approach proposed in this paper proved practicable and reliable. Also, the pseudo-steady state method developed here works well. It is time saving and suited for the analysis of the overall mass transfer coefficients with the reaction.

6. Notation

a_p	specific particle surface,=particle surface area (S_p)/particle volume (V_p), m^{-1}
a_r	ratio of catalyst activity, particle to powder $=(k_v)_{particle}/(k_v)_{powder}$
C_H,C_x	hydrogen and xylose concentration in solution, kmol/m^3
C_{Hs},C_{xs}	hydrogen and xylose concentration at catalyst particle surface, kmol/m^3
C_{x0}	xylose concentration in feeding, kmol/m^3
C_{xa},C_{xb}	xylose input and output concentration, sampled at valve f_a or f_b (see Fig. 1)
C_{xz}	xylose concentration at bed length z, kmol/m^3
d_p	particle diameter, mm
D_H, D_x	diffusivity of xylose and hydrogen in solution
k_v	intrinsic rate constant, give in Eq. (1), s^{-1}
K_G, K_L	overall mass transfer coefficient of H_2 and xylose, from bulk flow to surface, m/s
K_H	adsorption constant of hydrogen, give in Eq. (1), m^3/kmol
L	featured particle length, equal to $1/a_p$, m
P_H	partial pressure of hydrogen in bed, MPa
r_v	volumetric reaction rate, kmol/(m^3-cat s)
t_r	average residual time of liquid feed between point A and f_b (see Fig. 1), min
u_L	superficial liquid velocity, m/s

Greek symbols

α_H	hydrogen solving coefficient, kmol/(m^3MPa)
ϵ_p	porosity of activated layer
η_s	effectiveness factor defined in Eq. (2)
τ	torture factor of pores
ϵ_b	void fraction in bed
δ_L	featured length of activated layer, mm

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