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## EVALUATION OF TRICKLE BED REACTOR MODELS FOR A LIQUID LIMITED REACTION

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**Abstract-** The isothermal decomposition of hydrogen peroxide on a CuCr catalyst in a laboratory scale trickle bed reactor was used to test model predictions of the dependence of liquid reactant conversion on space time for different operating conditions. It is assured that the decomposition of hydrogen peroxide is a first order liquid-limited reaction. Comparison of model predictions and experimental data indicates that both external mass transfer effects and incomplete external catalyst wetting need to be accounted for. Dudukovic's (1977) approximate model for the catalyst effectiveness factor adequately simulates both effects.

### INTRODUCTION

Trickle-bed reactors, fixed beds of catalyst contacted by cocurrent downflow of gas and liquid, are used extensively for gas-liquid-solid catalyzed systems such as those encountered in various petroleum, petrochemical and chemical processes as well as in waste water treatment. Understanding the phenomena that govern the performance of trickle-bed reactors is essential to their design, scale-up and performance improvement. Modeling of trickle-bed reactors plays an important role in reaching such an improved understanding. Pressure drop, liquid holdup and liquid-catalyst wetting efficiency are hydrodynamic parameters which have to be accounted for in such a modeling effort together with the description of reaction kinetics and transport in catalyst particles. Most of the reported investigations in the literature have suggested a plug flow model for the liquid phase modified by considering some other factors such as external liquid hold up, external contacting, catalyst effectiveness, and so on. For example, Henry and Gilbert (1973) used a modified plug flow model which for a first order reaction takes the form below

$$\ln\left(\frac{1}{1-x}\right) = \frac{k_a h_l}{LHSV} \quad (1)$$

where  $h_l$  is external liquid hold up, LHSV is the liquid hourly space velocity and  $k_a$  is the first order rate constant (i.e., the apparent constant equal to the product of the true rate constant and the effectiveness factor  $k_a = k\eta$ ). Mears (1974) used a similar model which replaces the liquid hold up with the effective wetting of the external catalyst surface and the catalyst effectiveness factor. His equation is

$$\ln\left(\frac{1}{1-x}\right) = \frac{k\eta\eta_{ce}}{LHSV} \quad (2)$$

here  $\eta_{ce}$  is the external catalyst contacting efficiency (i.e. the fraction of the external catalyst area wetted by flowing liquid) and  $\eta$  is the catalyst effectiveness factor for the completely wetted catalyst particles that accounts only for internal transport effects.

An overall trickle bed effectiveness factor model was developed by Dudukovic (1977). In this model Dudukovic suggested that the effectiveness factor and partial surface wetting effects are coupled local phenomena. He incorporated both the external and internal partial wetting effects into the definition of the Thiele modules for nonvolatile, liquid-phase reactant limited reactions and arrived at the following formulation for the overall effectiveness factor of a partially wetted pellet,  $\eta_{TB}$ , which accounts for both external (film) and internal effects.

$$\eta_{TB} = \frac{\frac{\eta_{ce} \tanh(\frac{\eta_i \phi}{\eta_{ce}})}{\phi}}{1 + \frac{\phi}{Bi_m} \tanh(\frac{\eta_i \phi}{\eta_{ce}})} \quad (3)$$

Here  $\eta_i$  and  $\eta_{ce}$  are the internal and external fractional wetting, respectively, and  $Bi_m$  is the Biot number for liquid-solid mass transfer. Due to capillary forces,  $\eta_i$  is commonly assumed to be unity, and the reactor design equation for a first order reaction based on assumed plug flow of the liquid is:

$$\ln\left(\frac{1}{1-x}\right) = \frac{k\eta_{TB}}{LHSV} \quad (4)$$

When the external mass transfer resistance is negligible ( $Bi_m \rightarrow \infty$ ) and the Thiele modulus  $\phi$  is large, the trickle bed effectiveness factor,  $\eta_{TB}$ , is closely approximated by the relationship

$$\eta_{TB,\infty} = \eta_{ce}\eta \quad (5)$$

and the design equation (4) is reduced to equation (2). The catalyst wetting efficiency of the external catalyst surface,  $\eta_{ce}$ , can be calculated at atmospheric pressure using the correlation of El-Hisnawi *et al.* (1981).

$$\eta_{ce} = 1.617 Re_L^{0.146} Ga_L^{-0.071} \quad (6)$$

At high pressure the modification of El-Hisnawi *et al.* (1981) correlation recently reported by Al-Dahhan *et al.* (1995) can be used,

$$\eta_{ce} = 1.104 Re_L^{1/3} \left[ \frac{1 + [(\Delta P/Z)/\rho_L g]}{Ga_L} \right]^{1/9} \quad (7)$$

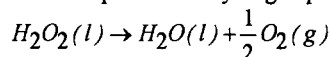
Catalyst effectiveness factor  $\eta$  is calculated using intrinsic and apparent kinetic data.

While the models represented by equation (1) and (2) have been utilized to correlate a limited number of industrial data, a rigorous test of the validity of these expressions has never been made. Moreover, the intuitively appealing more general model of Dudukovic (1977), *i.e.* equation (4), has not been experimentally tested.

The objective of this study was to test the ability of the presented models, especially the one resulting in equation (4), to predict the performance of a trickle bed reactor for a liquid limited reaction system of known kinetics and known catalyst effectiveness factor. The isothermal catalytic decomposition of hydrogen peroxide in water on CuCr catalyst extrudates was employed for this purpose.

### EXPERIMENTAL APPARATUS AND PROCEDURE

In order to test model predictability it was necessary to perform the reaction on a stable catalyst, confirm that it is first order in the liquid reactant and evaluate the intrinsic rate constant as well as the apparent rate constant (*i.e.* catalyst effectiveness factor) on the catalyst particles of the same size as those to be used in the trickle bed. As mentioned, the liquid phase decomposition of hydrogen peroxide



was chosen as a test reaction. Fourteen different catalyst preparations, including  $MnO_2$ ,  $CoMo$ ,  $NiO_2AlO_2$ ,  $Ni$ ,  $Pt$ ,  $Pd$ ,  $NiO$ , and  $CuCr$  were screened for suitable catalyst activity, and extensive (one week or longer) experimentation was carried out with each catalyst to determine its stability. Copper chromite 1/16" (Engelhard) catalyst was found to be the best catalyst that stayed stable during repeated runs over a long period of time as illustrated in Figure 1.

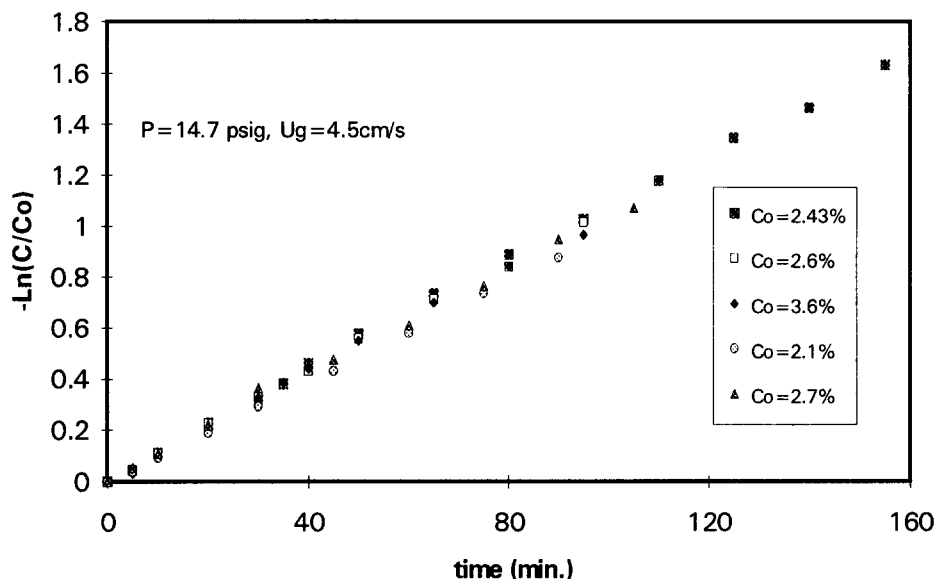


Figure 1. Catalyst stability and kinetic test in a basket reactor(1/16"extrudate)

First order decomposition was confirmed (Wu, 1994) so that the rate form can be represented by

$$-r_A = kC_A \quad (8)$$

Studies in a slurry system using crushed small catalyst particles revealed the following value for the intrinsic rate constant

$$k = 1.27 \cdot 10^8 \exp(-10,525 / RT) \quad 1/\text{min.} \quad (9)$$

The apparent kinetic constant on a 1/16" extrudate was evaluated on a completely wetted catalyst in a basket reactor as

$$k_a = 1.48 \cdot 10^5 \exp(-7,404 / RT) \quad 1/\text{min.} \quad (10)$$

This corresponds to an effectiveness factor of  $\eta = 0.23$  at room temperature.

The trickle bed experiments were performed in the facility which was described in detail elsewhere (Al-Dahhan and Dudukovic, 1995). Copper chromite 1/16" (Engelhard) extrudates were packed in a 2.2 cm diameter tube to a height of 30 cm with glass beads (3mm diameter) on both sides to a total reactor length of 50 cm. Catalyst and reactor properties are listed in Table 1. The range of operating conditions studied are reported in Table 2. Due to a dilute feed it was possible to conduct all trickle bed experiments isothermally at room temperature of 22°C (295 K).

**REACTOR MODELS**

Since our intent was to assess the ability of the model proposed by Dudukovic (1977) to predict trickle bed performance, all model parameter had to be evaluated independently. Both the intrinsic rate constant and apparent rate constant are experimentally determined ( $\phi = 3.59$ ). The Biot number in equation (3) requires the knowledge of liquid-solid mass transfer coefficient. At each liquid flow rate this was obtained from the correlation of Lakota and Levec (1990). Hence, comparison of the predictions based on equation (4) and data can now be made. A limiting case of the model is the situation when external mass transfer resistance is negligible ( $Bi_m \rightarrow \infty$ ) and these predictions can be also plotted. For completeness, we have also tested the predictions of equation (1) and equation (2) against data. In addition we tested the form of the effectiveness factor suggested by Beaudry et al. (1987) which was recently successfully used to interpret the data for a gas limited reaction. These authors represented the catalyst particles as an assembly of externally half-wetted, totally wetted and completely unwetted slabs and proposed the overall effectiveness factor for the assembly as

$$\eta_a = (1 - \eta_{ce})^2 \eta_d + 2 \eta_{ce} (1 - \eta_{ce}) \eta_{1/2} + \eta_{ce}^2 \eta_{ow} \quad (11)$$

For a liquid limited reaction  $\eta_d = 0$ ,  $\eta_{ow}$  and  $\eta_{1/2}$  is the overall effectiveness factor of a completely wetted pellet and of a pellet of twice the actual modulus i.e.  $\phi_{1/2} = 2\phi$ , respectively. The reactor model then can be written as equation (4) with  $\eta_a$  replacing  $\eta_{TB}$ .

**RESULTS AND DISCUSSION**

The decomposition of hydrogen peroxide was performed in the described laboratory trickle bed reactor at different feed concentration and at different pressures. As shown in Figure 2, the feed concentration

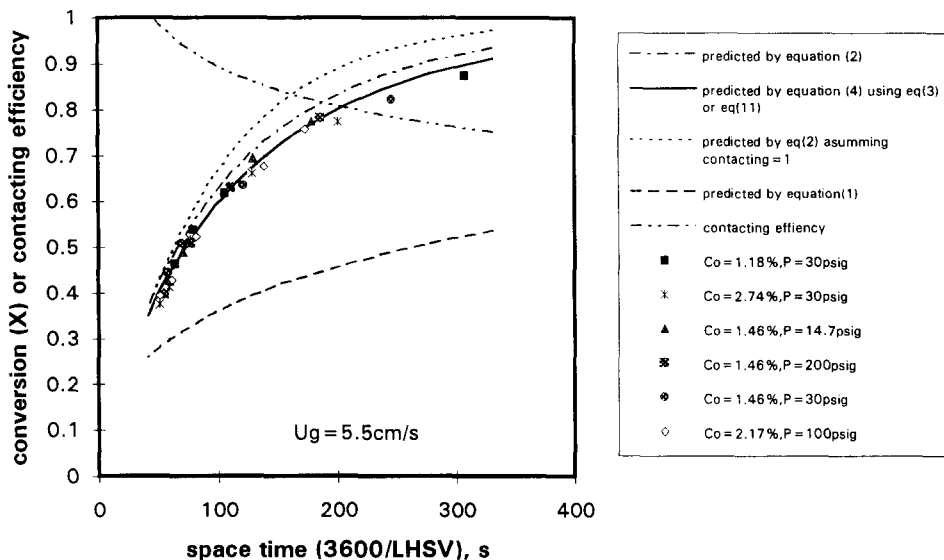


Figure 2. Comparison of different model predictions and experimental data

of hydrogen peroxide varied from 1.17% to 2.74%, and pressure was changed from atmospheric to 13.6 atm for different experiments. It is obvious that conversion is independent of feed concentration which is expected for a first order liquid-limited reaction. Conversion is also clearly independent of pressure, this is in agreement with the recent findings of Al-Dahhan and Dudukovic (1995) who showed that while contacting efficiency at fixed liquid mass velocity increases with pressure, such increase is marginal at low gas velocity. Over the range of operating conditions of this study equations (6) and (7) predict essentially the same contacting efficiency as the pressure effect is not pronounced at low gas velocity. Contacting efficiency does not increase more than 5% when pressure changes from 30 to 200 psig according to equation (7). This is not sufficient to cause an observable changes in conversion.

Comparison of Dudukovic's model prediction and experimental results is shown in Figure 2 also. The prediction of the model is improved when external mass transfer resistance is accounted for. Hence equation (4) together with equation (3) predicts experimental results better than equation (2) does.

Comparison of predictions of different models and experimental data is also illustrated in Figure 2. Equation (1) underpredicts the data dramatically which is to be expected since holdup is not a fundamental variable. Equation (2) overpredicts the data somewhat indicating that external transport resistance needs to be accounted at large Thiele modules which is expected. Utilizing contacting efficiency of unity,  $\eta_{ce}=1$ , overpredicts the data considerably clearly illustrating the need for properly accounting for incomplete particle wetting. Finally, equation (4) with either  $\eta_{TB}$  from equation (3) or with  $\eta_a$  from equation (11) predicts experimental results within 10% error. It turns out that the formulation for the overall effectiveness factor introduced by Dudukovic (1977) and Beaudry *et al.* (1987) are in good agreement at large moduli.

## CONCLUSIONS

The results presented above confirm that both contacting efficiency and external transport resistance need to be accounted for liquid limited reactions at high Thiele moduli. The models introduced by Dudukovic (1977) and Beaudry *et al.* (1987) which properly account for these effects, are capable of predicting trickle bed performance for liquid limited reactions of known kinetics. Other more empirical models do not fare as well.

## ACKNOWLEDGMENT

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## NOTATION

- $Bi_m$  = Biot number for mass transfer =  $k_{LS}(V_p / S_x) / D_e$   
 $C, C_0$  = reactant and reactant feed concentration, mol/m<sup>3</sup>  
 $d_p$  = particle diameter, m  
 $D_e$  = effective diffusivity, m<sup>2</sup>/s  
 $g$  = gravitational acceleration, m/s<sup>2</sup>  
 $Ga_L$  = Galileo number =  $d_p^3 \rho_l^2 g / \mu_l^2$   
 $h_l$  = external liquid holdup  
 $k, k_a$  = intrinsic and apparent, first-order kinetic rate constant, respectively, 1/min  
 $k_{LS}$  = liquid-solid mass transfer coefficient, m/s  
 $L$  = length of catalyst bed, m  
 $LHSV$  = liquid hourly space velocity, m/m-cat\*hr =  $u_l / L$   
 $Re_L$  = Reynolds number of the liquid phase =  $d_p u_l / \nu$   
 $S_x$  = external catalyst area, m<sup>2</sup>  
 $u_l$  = liquid superficial velocity, m/s  
 $V_p$  = catalyst particle volume, m<sup>3</sup>  
 $x$  = conversion =  $1 - C/C_0$

## Greek Letters

- $\eta$  = single fluid-phase catalyst pellet effectiveness factor =  $\tanh \phi / \phi$   
 $\eta_{ce}$  = fraction of external catalyst surface which is wetted with active liquid  
 $\eta_i$  = fraction of internal catalyst void volume which is wetted  
 $\eta_a$  = global (overall) effectiveness factor, defined by Eqn. 11  
 $\eta_{ow}$  = global effectiveness factor for completely wetted pellet

- $\eta_{TB}$  = global (overall) effectiveness factor, defined by Eqn.3  
 $\rho_e$  = liquid density, kg/m<sup>3</sup>  
 $\mu_l$  = liquid viscosity, kg/m/s  
 $\nu$  = liquid kinematic viscosity, m<sup>2</sup>/s  
 $\phi$  = Generalized Thiele Modulus =  $V_p / S_x (k / D_e)^{0.5}$

**Table 1 : Catalyst and Reactor Properties**

<u>Catalyst Properties</u>		<u>Reactor Properties</u>	
Active metal	23% CuCr.	Total length	50 cm
Catalyst support	alumina	Catalyst length	30 cm
Packing shape	trilobe	Diameter	2.2 cm
Packing dimensions (cm)	0.13 x 0.56		
Surface area (m <sup>2</sup> / g)	120		
Total pore volume (cm <sup>3</sup> / g)	0.36		
Pellet density $\rho_p$ (g / cm <sup>3</sup> )	1.05		

**Table 2 : Range of Operating Conditions**

Temperature	22 <sup>o</sup> C
Pressure	14.7 - 200 psig (1 -15 atm.)
Concentration of hydrogen peroxide	1.17 - 2.78 % (w/w)
Superficial Gas Velocity (Mass Velocity)	3.8 - 14.4 cm/s (4.7x10 <sup>-2</sup> -18x10 <sup>-2</sup> kg/m <sup>2</sup> s)
Superficial Liquid Velocity (Mass Velocity)	0.09-0.5 cm/s (0.9 - 5 kg/m <sup>2</sup> s)

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