

Determination of Wetting Efficiencies for a Trickle-Bed Reactor at High Temperatures and Pressures

Wetting efficiencies for trickle-bed reactors are needed at conditions typical of industrial operations. A theoretical approach was developed which allows wetting efficiencies to be determined for trickle-bed reactors under reaction conditions. The hydrogenation of biphenyl was chosen as a model reaction. Wetting efficiencies were determined for this system at 295 °C and 5.2 MPa. Values ranged from 0.0 to 0.89.

Many industrial trickle-bed reactors operate at high temperatures and pressures where partial vaporization of the liquid feed occurs, yet most of the experimental work has been conducted at or near ambient conditions using nonvolatile liquid feeds. Only a handful of reported experiments exist in which the possible influence of partial wetting on reactor performance is shown for conditions typically found in industry (Mears, 1971; Montagna and Shah, 1975; Paraskos et al., 1975).

The reaction rate in a trickle-bed reactor can be written as a weighted average of the rate on the liquid-covered surface and the rate on the dry surface

$$r = f\eta_l(r_i)_l + (1 - f)\eta_g(r_i)_g \quad (1)$$

where $\eta_l(r_i)_l$ and $\eta_g(r_i)_g$ are the reaction rates in the liquid phase over the wetted catalyst and the gas phase over the dry catalyst, respectively, in terms of the intrinsic rates and effectiveness factors. For a second-order reaction



the rate expression becomes

$$r = f\eta_l k_1 C_A^l C_B^l + (1 - f)\eta_g k_g C_A^g C_B^g \quad (3)$$

For simplicity, assuming a plug flow model gives

$$r = \frac{-dn_A}{dW} \quad (4)$$

where species A is the limiting reactant. The molar flow rate of A can be written in terms of the conversion as

$$n_A = n_A^0(1 - X) \quad (5)$$

Thus

$$dn_A = -n_A^0 dX \quad (6)$$

Combining (3), (4), and (6) leads to

$$n_A^0 \frac{dX}{dW} = f\eta_l k_1 C_A^l C_B^l + (1 - f)\eta_g k_g C_A^g C_B^g \quad (7)$$

Integrating over the catalyst bed gives

$$W = \int_0^{X_f} \frac{n_A^0 dX}{f\eta_l k_1 C_A^l C_B^l + (1 - f)\eta_g k_g C_A^g C_B^g} \quad (8)$$

Wetting efficiencies can be determined from experimental trickle-bed data by trial and error using (8) and an equation of state to obtain gas- and liquid-phase concentrations provided $\eta_l k_1$ and $\eta_g k_g$ are known. The inlet molar flow rate of the limiting reactant, n_A^0 , exit conversion, X_f , and the amount of catalyst, W , are known; thus, the wetting efficiency is the only unknown parameter in (8). This approach assumes that the wetting efficiency remains constant throughout the reactor which is consistent with the results presented by Tsukamoto et al. (1982) and Ruecker et al. (1985).

If the reaction is performed under conditions such that no liquid phase exists, then $f = 0$ and (8) reduces to

$$\eta_g k_g = \frac{1}{W} \int_0^{X_f} \frac{n_A^0 dX}{C_A^g C_B^g} \quad (9)$$

The inlet molar flow rate of the limiting reactant, the exit conversion, and the amount of catalyst are known; hence a simple integration yields $\eta_g k_g$. A value for $\eta_l k_1$ can be obtained in a similar manner by performing an experiment in a liquid-full reactor or by using a trickle-bed reactor at high enough liquid flow rates to ensure complete liquid coverage of the catalyst. In either case $f = 1$ and (8) can be rearranged to give

$$\eta_l k_1 = \frac{1}{W} \int_0^{X_f} \frac{n_A^0 dX}{C_A^l C_B^l} \quad (10)$$

This integral has to be solved numerically by employing an equation of state and a suitable technique such as collocation integration (Mensik, 1985). Values of the wetting efficiency can now be obtained from (8) for trickle-bed experiments provided that the temperature, pressure, and catalyst bed are the same as those used to determine $\eta_l k_1$ and $\eta_g k_g$.

We have used the hydrogenation of biphenyl as a model reaction and conducted a series of experiments in an effort to determine wetting efficiencies in a trickle-bed reactor at 295 °C and 5.2 MPa where the liquid feed is partially volatile. The details of the experimental setup are presented elsewhere (Ruecker, 1985). The catalyst bed was preflooded, and the same bed was used in the study.

The experiment was started at a hydrogen-to-liquid feed ratio of 5330 sccm of H_2 to 6 mL/min of liquid feed. Flash calculations, which employ various equations of state and Gibbs free-energy minimization techniques (Ruecker, 1985), predict that no liquid phase should be present at these conditions; thus, a value for $\eta_g k_g$ can be obtained from the exit conversion by using (9). The measured conversion of 0.96 resulted in a value of $\eta_g k_g = 0.058 \text{ L}^2/(\text{g} \cdot \text{mol} \cdot \text{g of catalyst} \cdot \text{min})$. After $\eta_g k_g$ was determined, the hydrogen flow rate was lowered and a sample collected once the system had reached steady state. The results of this experiment are shown in Figure 1. The highest hydrogen flow rate corresponds to an all-gas-phase system, but flash calculations predict that both a gas and a liquid phase are present in the other experiments.

The existing equipment could not be easily modified to be operated in liquid-full mode, and the liquid flow rate was probably not high enough to ensure complete liquid coverage at even the lowest hydrogen flow rate, so none of the experimental data points can be directly used in (10) to evaluate $\eta_l k_1$. An estimate for $\eta_l k_1$ was obtained by using a hypothetical data point based on the experimental results. The liquid-phase concentration of biphenyl can be written in terms of the total liquid-phase concentration, flash parameters, and total component molar flow rates by using a series of simplifying relations

$$C_j^l = x_j C_T^l \quad (11)$$

$$x_j = \alpha_j z_j \quad (12)$$

$$z_j = \frac{n_j}{n_T} \quad (13)$$

and

$$\alpha_j = (1 - \psi(1 - K_j))^{-1} \quad (14)$$

where

$$\psi = \frac{n_T^v}{n_T} \quad (15)$$

and

$$K_j = \frac{y_j}{x_j} \quad (16)$$

Then

$$C_{BP}^l = \alpha_{BP} n_{BP} \left(\frac{C_T^l}{n_T} \right) \quad (17)$$

Then (10) becomes

$$\eta_l k_l = \frac{1}{W} \int_0^{X_f} \frac{n_{BP}^0 dX}{\alpha_{BP} n_{BP} \left(\frac{C_T^l}{n_T} \right) C_H^l} \quad (18)$$

The total molar flow rate of biphenyl can be written in terms of the conversion as

$$n_{BP} = n_{BP}^0 (1 - X) \quad (19)$$

Substituting into (19) yields

$$\eta_l k_l = \frac{1}{W} \int_0^{X_f} \frac{dX}{\alpha_{BP} C_H^l \left(\frac{C_T^l}{n_T} \right) (1 - X)} \quad (20)$$

The hydrogen solubility, C_H^l , remains essentially constant throughout the reactor for all the experiments at ~ 0.28 g-mol/L, so it can be treated as a constant and be moved outside the integral. The exit conversion, X_f , and $\xi = n_T / (\alpha_{BP} C_T^l)$ can be plotted vs. the vapor fraction, ψ , for all the experiments. Extrapolating to $\psi = 0$ in Figures 2 and 3 gives values for X_f and ξ at a hypothetical point where the vapor fraction is zero; thus, the catalyst should be completely covered by the liquid. It should be noted that extrapolations of both curves are somewhat flat in the region $\psi = 0-0.5$, indicating that complete wetting will occur much above $\psi = 0$. Using the values obtained from Figures 2 and 3 and assuming that ξ remains constant throughout the reactor leads to $\eta_l k_l = 0.0016$ L²/(g-mol of catalyst-min). Values of the wetting efficiency can now be obtained from the data shown in Figure 1 by using the values obtained for $\eta_l k_l$ and $\eta_g k_g$ and (8). The values obtained are shown in Figure 4 as a function of the vapor fraction. The data can be correlated by a quadratic fit

$$f = 1.00 + 0.14\psi - 1.17\psi^2 \quad (21)$$

The model presented here was tested by trying to predict the conversion for another set of experiments performed at the same conditions. The liquid feed rate was again held constant at 6 mL/min. This time the hydrogen flow rate was also held constant at a value of 600 sccm, and nitrogen was used to adjust the total gas flow rate. Predicted conversions can be obtained for these experiments from (8) provided values for f are known. Wetting efficiencies can be predicted using equation (21), leaving X_f as the only unknown, since the values for $\eta_l k_l$ and $\eta_g k_g$ should be the same as for the previous experiments. The results of the variable nitrogen flow rate experiments are

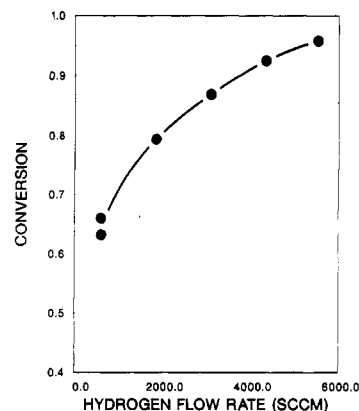


Figure 1. Change in conversion with hydrogen flow rate.

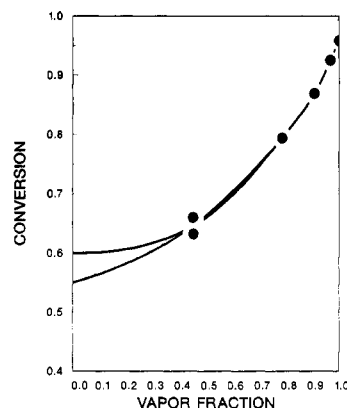


Figure 2. Extrapolation of the exit conversion to $\psi = 0$.

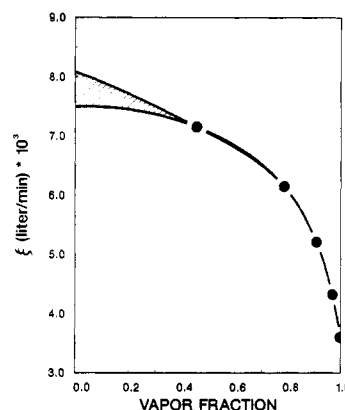


Figure 3. Extrapolation of ξ to $\psi = 0$.

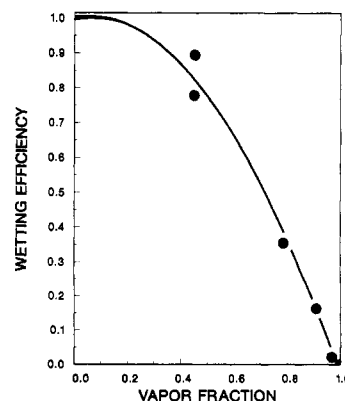


Figure 4. Correlation of experimental wetting efficiencies with vapor fraction.

shown in Figure 5 along with the conversions predicted by (8). It is interesting to note that in this set of experiments

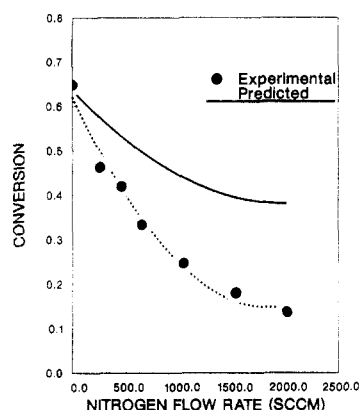


Figure 5. Changes in predicted and experimental conversions with nitrogen flow rate.

the conversion decreased with increasing gas flow rate, while the conversion increased with increasing gas flow rate for the variable hydrogen experiments. Although (8) does not match the experimental data exactly, it correctly predicts the decreasing trend, and the curve has the same shape as the experimental data. The predicted conversions are always larger than the experimental values. The difference between these two curves could be due to inhibiting effects of the nitrogen. It is possible that the nitrogen reversibly adsorbs on the catalyst surface, thus temporarily blocking active sites which would lower the observed conversion.

Conclusions

The extrapolation to $\psi = 0$ used to obtain a hypothetical data point in which the liquid coverage is assumed to be complete may not be justified, so the sensitivity of the calculated wetting and predicted conversions was tested by assuming various values of ηk_l . The assumed value had an effect on the calculated wetting efficiency and the resulting correlation (eq 22) but it did not affect the predicted conversions for the variable nitrogen experiments. The correlation given to predict wetting efficiencies may not be justified due to the sensitivity with respect to ηk_l , which was not determined accurately, yet the technique is significant as shown by its ability to correctly predict the decrease in conversion with increasing gas flow rate for the variable nitrogen experiments.

The theoretical approach presented makes it very simple to extract wetting efficiencies from experimental data provided experiments can be conducted at the extreme values of $f = 0$ and $f = 1$. Once the values for ηk_l and ηk_g have been determined for a given temperature, pressure, and catalyst bed, it is possible to quickly obtain wetting efficiencies for experiments at other flow rates and feed compositions. This procedure makes it possible to experimentally determine wetting efficiencies under reaction conditions for a variety of chemical systems and is not limited to low temperatures and pressures. It may be argued that at high liquid flow rates all catalyst internal probes would be saturated by the liquid by capillary action and the difference in conversion will be due to external mass-transfer resistances on the dry and wet catalyst particles. At the present time we are investigating this possibility by employing a different reaction system where external resistances will be negligible.

Flash calculations may not be sufficient to explain the dry and wet catalyst since inside of catalyst pores may be completely wetted due to capillary condensation. Nevertheless, in the absence of physicochemical data relating the effects of capillary condensation on vapor-liquid equilibrium, the technique presented is feasible.

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Nomenclature

C = concentration, g-mol/L
 f = wetting efficiency, dimensionless
 k = rate constant, $L^2/(g\text{-mol}\cdot g \text{ of catalyst}\cdot \text{min})$
 K_j = distribution coefficient of species j , dimensionless
 K_N = nitrogen equilibrium adsorption coefficient, L/g-mol
 n = molar flow rate, g-mol/min
 r = observed reaction rate, g-mol/(g of catalyst·min)
 r_i = intrinsic reaction rate, g-mol/(g of catalyst·min)
 W = amount of catalyst, g
 X = conversion, dimensionless
 x_j = liquid mole fraction of species j , dimensionless
 y_j = gas mole fraction of species j , dimensionless
 z_j = total mole fraction of species j , dimensionless

Greek Symbols

$\alpha_j = x_j/z_j$, dimensionless
 η = effectiveness factor, dimensionless
 ψ = vapor-to-feed molar ratio, dimensionless
 $\xi = n_T/\alpha_{BP}C_T$, L/min

Superscripts

g = gas
 l = liquid
 0 = initial
 v = vapor

Subscripts

BP = biphenyl
 f = final
 g = gas
 H = hydrogen
 j = species j
 l = liquid
 N = nitrogen
 T = total

Literature Cited

- Mears, D. E. *Chem. Eng. Sci.* **1971**, *26*, 1361.
- Mensik, M. A. MS Thesis, Texas A&M University, College Station, 1985.
- Mills, P. L.; Dudukovic, M. P. *AIChE J.* **1981**, *27*, 893.
- Montagna, A. A.; Shah, Y. T. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 479.
- Paraskos, J. A.; Frayer, J. A.; Shah, Y. T. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 315.
- Ruecker, C. M. MS Thesis, Texas A&M University, College Station, 1985.
- Ruecker, C. M.; Mensik, M. A.; Akgerman, A. *Chem. Eng. Commun.* **1986**, *41*, 279.
- Tsukamoto, T.; Morita, S.; Okada, J. *Chem. Pharm. Bull.* **1982**, *30*, 1539.

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