ELSEVIER

Catalysis Today 24 (1995) 103–109

CATALYSIS TODAY

Continuous hydrogenation of adiponitrile on Raney nickel in a slurry bubble column

D. Gavroy *, C. Joly-Vuillemin, G. Cordier, P. Fouilloux, H. Delmas

'Three-phase catalytic reactors', UMR 45 CNRS/Rhône–Poulenc, 24, avenue Jean Jaurès, 69153 Décines Charpieu Cedex, France

Abstract

An experimental study of the catalytic hydrogenation of adiponitrile in a mini-plant with a continuously operated slurry draft-tube bubble column is discussed. The purpose of this work is to determine the influence of operating parameters on the performance of the reactor, and to develop a complete model to describe its behaviour.

The following basic information was first obtained:

- hydrodynamic data; a mock-up of the same scale as the reactor is built to measure the characteristics of the fluid flow.
- intrinsic kinetics data; the Langmuir–Hinshelwood model is chosen, supposing surface reaction limitation and competitive adsorption between hydrogen and nitriles. This correctly describes the experimental data.

From this first information, a model supposing well-mixed liquid phase is developed. It is not a completely predictive model, since two parameters have to be estimated: the volumetric liquid-phase mass transfer coefficient and the deactivation parameter. This complete model is available representing experimental data with good accuracy.

1. Introduction

In a comprehensive study of a three-phase catalytic reaction process in a packed or slurry bubble column reactor, many different elements are requested for reactor design and modelling. These are namely reaction kinetics, catalyst deactivation, hydrodynamics (phase holdups, circulation and axial dispersion), mass transfer (liquid–solid, gas–liquid and intraparticle diffusion). These different aspects of the reaction process cannot be investigated with the same equipment. For example kinetics must be derived in a perfectly stirred batch reactor avoiding any heat or mass transfer limitations. On the other hand hydrodynamics could be hardly investigated in the actual reactor and a representative mock-up is highly preferable because it allows intrinsic measurements, while using the true reaction medium (same liquid and solid phases). In the case of hydrogenations, the problem of reliable gas–liquid mass transfer measurements is raised by the difficult determination of hydrogen concentration in the liquid phase. In this paper, different ways to achieve a complete modelling of the continuous adiponitrile hydrogenation on Raney nickel are presented and discussed.

2. Experimental

Hydrogenations were carried out in the experimental setup outlined in Fig. 1. The bubble column reactor was operated continuously with respect to the gas and the liquid phases. Raney

---

* Corresponding author.

SSDI 0920-5861(95)00003-8

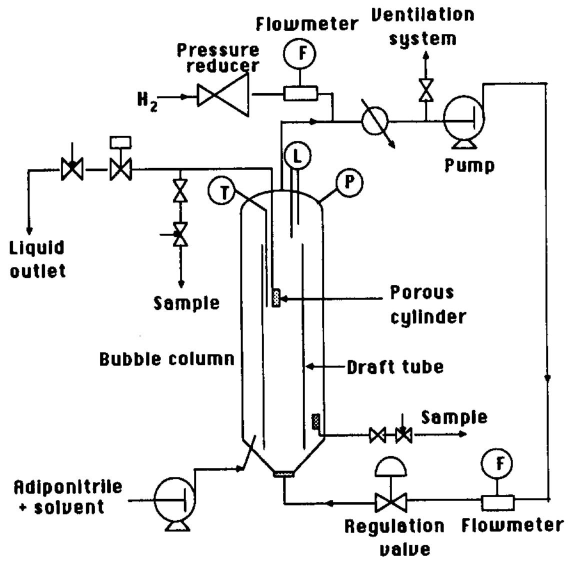


Fig. 1. Schematic flow sheet of the pressurized bubble column.

nickel catalyst was introduced in the reactor before beginning the hydrogenation and kept inside with porous systems during the experiment. A jacket around the reactor maintained a constant reactor temperature. The stainless steel bubble column with a conical bottom was 0.057 m ID and 1 m in height. A 0.03 m ID stainless steel draft tube 0.75 m in height was coaxially located inside the column. Hydrogen was introduced at the bottom of the reactor through a porous plate. Solvent vapor and excess hydrogen gas entered a condenser. The condensate was separated from the remaining gas and returned to the reactor. Hydrogen was recycled by a membrane pump. Its flow rate was controlled by a regulation valve and measured by a mass flowmeter. To supply the gas consumed by the reaction and to maintain a constant pressure in the reactor, a controlled quantity of hydrogen was drawn from a gas network. Adiponitrile and solvent were fed into the reactor by means of a plunger pump. The liquid level in the bubble column was regulated by conductivity probes which controlled a pneumatic valve. Samples could be taken at the top and at the bottom of the column and analyzed by gas chromatography. The dissolved hydrogen concentration was measured by transferring liquid in a vessel under vacuum: hydrogen was desorbed by shaking the vessel until equilibrium was achieved. The quantity of dissolved hydrogen was determined by a mass balance of the gas phase combined with the equilibrium law.

To validate the geometry of the stainless bubble column and to determine hydrodynamic data, a PVC mock-up at the same scale as the reactor was built. It is schematically illustrated in Fig. 2.

There was no net inflow or outflow of liquid in the transparent bubble column but, as the liquid flow rate in the pressurized bubble column was lower than 0.4 mm s^{-1}, the hydrodynamic data determined under batch-liquid operating conditions could be applied to the pressurized reactor. Experiments were carried out at atmospheric pressure and room temperature. Nitrogen was used as the gas phase. Its density under these conditions was similar to that of hydrogen under reaction conditions (2 MPa and 353 K). The results obtained with nitrogen could be applied to the pressurized reactor, as the effect of pressure on gas holdup is linked to the gas density ([1]). Distilled water and the reaction solvent were used as the liquid phase. The properties of the reaction solvent are as follows: density 877 kg m^{-3} at 293 K and 825 kg m^{-3} at 353 K, viscosity $6.4 \cdot 10^{-3}$ Pa s at 293 K and $1.3 \cdot 10^{-3}$ Pa s at 353 K, surface tension 0.033 N m^{-1} at 293 K.

The solid phase consists of pyrophoric Raney nickel particles (average diameter 15 μm and

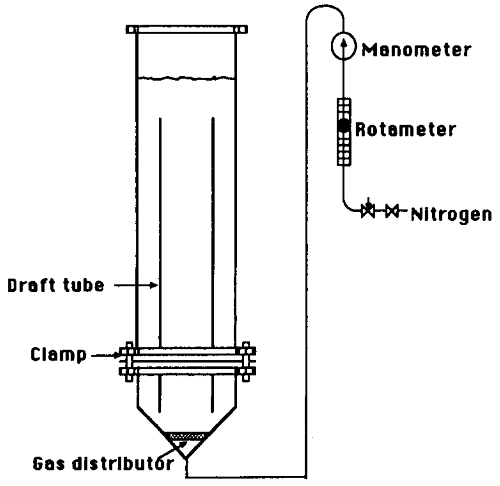


Fig. 2. PVC mock-up of bubble column.

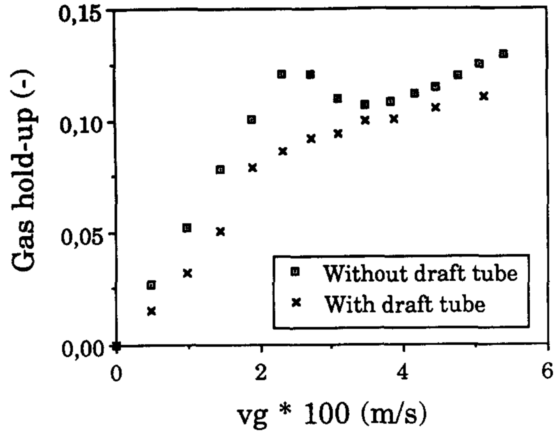


Fig. 3. Influence of the draft tube on gas holdup in the reaction solvent.

porosity 0.39). The alloy density is 7500 kg m^{-3} and the particle settling velocity in the reaction solvent at 293 K is $7.7 \cdot 10^{-5}$ m s^{-1} (according to Kozeny–Carman relation).

The gas velocity was adjusted to 0–0.06 m s^{-1}, based on the cross-sectional area of the outside column. The flow pattern and the suspension of solid were observed visually.

The overall gas holdup ϵ_g was calculated from the clear-liquid height and the height of the bubbly liquid, which were measured visually. The apparent liquid circulation rate between the draft tube and the annulus was measured by thermal tracing.

To develop a kinetic model of the adiponitrile hydrogenation, experiments were carried out in a 500 cm^3 mechanically stirred batch reactor which was operated at constant temperature and pressure. The initial adiponitrile concentration was varied from 0.1 to 2.5 kmol m^{-3}, the temperature was between 333 K and 373 K and the reactor pressure ranged from 1.5 to 5 MPa. Concentration versus time profiles were obtained from chromatography analyses of the samples taken during the reaction. The hydrogen consumption was calculated from the variation of the pressure in a storage vessel. It was checked that experiments were performed without any transfer limitations and any catalyst deactivation.

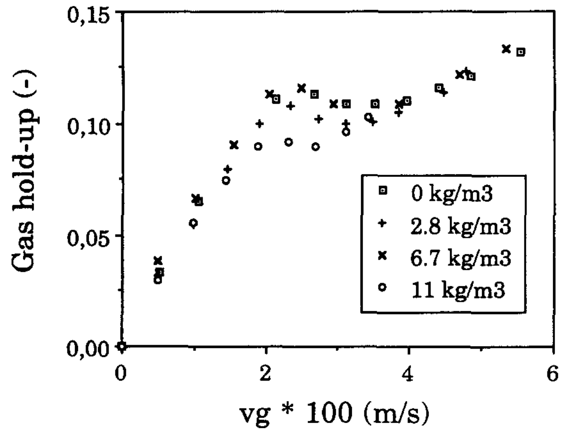


Fig. 4. Influence of the solid on gas holdup in the reaction solvent in the simple bubble column.

3. Hydrodynamics

The reaction solvent is a less coalescing liquid than water. The spherical bubbles were smaller and more numerous so that the gas holdup was larger. Fig. 3 shows that the gas holdup decreases in the churn-turbulent flow regime in the bubble column without a draft tube. When the tube was introduced in the column, this phenomenon disappeared. A front which separated the bubble-free liquid from the bubbly liquid appeared in the annulus. The bubble penetration depth increased when the gas velocity increased until reaching the bottom of the draft tube. The overall gas holdup was lower because the bubble rise velocity was increased by supplementary liquid circulation rate for a given gas velocity. No correlation predicted correctly the gas holdup in the reaction solvent.

The conical shape of the bubble column bottom made the suspension of solid particles easier. The complete suspension could be considered to be achieved at 0.035 m s^{-1} for solid loadings less than 11 kg m^{-3}.

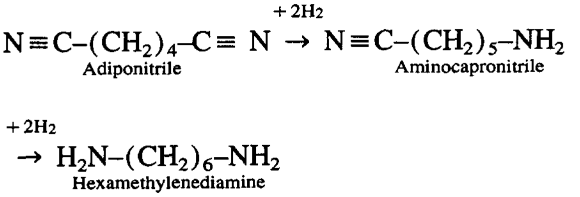
Fig. 4 shows the influence of solid loading on ϵ_g for the reaction solvent in the simple bubble column. For low concentrations (2.8 and 6.7 kg m^{-3}), ϵ_g was not affected. The decrease of ϵ_g for the churn-turbulent flow regime was also observed. On the contrary for greater solid loadings, ϵ_g was lower than that without solid particles, except when the first slugs appeared in the column.

In the draft tube bubble column, no influence of catalyst loading could be shown.

The liquid circulation rate increased with the gas velocity. It was between 0.2 and 0.25 m s^{-1} in the homogeneous flow regime.

4. Kinetics

Preliminary experiments showed that the hydrogenation of adiponitrile (ADN) to hexamethylenediamine (HMD) could be represented by two consecutive reactions with aminocapronitrile (ACN) as the intermediate product. With appropriate conditions, a high selectivity (>98%) was reached so that secondary reactions might be neglected.



$$\underset{\text{Adiponitrile}}{N{\equiv}C{-}(CH_2)_4{-}C{\equiv}N} \xrightarrow{+2H_2} \underset{\text{Aminocapronitrile}}{N{\equiv}C{-}(CH_2)_5{-}NH_2} \xrightarrow{+2H_2} \underset{\text{Hexamethylenediamine}}{H_2N{-}(CH_2)_6{-}NH_2}$$

A previous study based on initial rates ([2]) showed that the experimental data were correctly represented by the Langmuir–Hinshelwood formalism.

The utilization of complete kinetics with the help of a dynamic simulation software package showed the best accuracy of the competitive model which assumed that nitrile and hydrogen were adsorbed on the same sites. A deeper analysis of the parameter estimation showed the uncomplete determination of the adsorption constants, unlike rate constants which are unambiguously estimated. These points are detailed by [3].

5. Continuous hydrogenation of adiponitrile

Several hydrogenations in the continuous pressurized draft tube bubble column have been carried out with different operating conditions. The influence of the catalyst loading and the feed flow rate of adiponitrile on the reactor performance was studied. The temperature, the pressure and the volume in the bubble column were maintained constant. Depending on the operating conditions, two kinds of runs were obtained: reactions without deactivation for which the hydrogen consumption rapidly became constant during the run, and reactions with deactivation for which the hydrogen consumption decreased with time.

5.1. Reactor modelling

The reactor was considered to be perfectly mixed because the temperatures at the top and at the bottom of the column were identical and the differences of concentration between the samples taken at the top and those cut off at the bottom were less than 15%.

The differential equations for ADN, ACN and hydrogen were obtained from a mass balance where r_j was the rate of reaction j whose expression was detailed by [3].

$$\frac{dC_{ADN}}{dt} = -\Phi r_1 \cdot \frac{m}{(1-\epsilon_g)V_R} + \frac{Q}{(1-\epsilon_g)V_R} \cdot (C_{ADN,e} - C_{ADN}) \quad (1)$$

$$\frac{dC_{ACN}}{dt} = \Phi(r_1 - r_2) \cdot \frac{m}{(1-\epsilon_g)V_R} - \frac{Q}{(1-\epsilon_g)V_R} \cdot C_{ACN} \quad (2)$$

$$\frac{dC_{H2,l}}{dt} = -2 \cdot \Phi(r_1 + r_2) \cdot \frac{m}{(1-\epsilon_g)V_R} + k_l a \cdot (C^*_{H2,l} - C_{H2,l}) - \frac{Q}{(1-\epsilon_g)V_R} \cdot C_{H2,l} \quad (3)$$

The liquid–solid mass transfer was not a limiting step and it was checked a posteriori that the reaction was not limited by the internal transfer. Yet two parameters in the global mass balance had to be identified: the volumetric gas–liquid mass transfer, $k_l a$, and the deactivation function, Φ, which was the factor which multiplied the kinetic constants in the kinetic expressions.

5.2. Determination of k_la

5.2.1. Chemical method

This method was based on reaction modelling. Before beginning optimization from experimental data, it was important to study the parameter sensitivity by carrying out some simulations at different operating conditions, and for different values of k_la. The conclusions were as follows:

— When the mass of catalyst was high compared to the adiponitrile feed, nitrile conversion was nearly complete and hence the concentrations of ADN and ACN were low and measured with poor accuracy. The volumetric mass transfer coefficient had less influence on the conversion. Only a minimum value of k_la could be estimated from ADN and ACN concentrations. On the contrary, dissolved hydrogen concentration was very sensitive to k_la variations and its deviations were measurable (Fig. 5a and 5b).

— For high feed adiponitrile concentrations, k_la had a strong influence on ADN and ACN concentrations which were higher and consequently more accurately measured. Its determination became possible through experimental values of C_{ADN} and C_{ACN}. The time necessary to reach a steady state was also found to be a good indicator to assess k_la. It could vary from several minutes to three hours. Dissolved hydrogen concentration was influenced by k_la but its values were too low to be correctly assessed by the method used (Fig. 6a and 6b).

When the conversion was very low, a deactivation phenomenon was sometimes observed and k_la optimization became impossible. Only high conversion experimental results were therefore usable. The dissolved hydrogen concentration was the most appropriate data to estimate k_la. For instance, at a gas velocity of $1.3 \cdot 10^{-2}$ m s^{-1}, the volumetric gas–liquid mass transfer was about 0.05 s^{-1} (±10%).

5.2.2. Physical method

This consisted of measuring the variation of dissolved hydrogen concentration with time in a non-reacting liquid-batch process. This technique was similar to that performed in mechanically stirred reactors in which the variation of the pressure with time was followed. Yet it was difficult to carry it out in a bubble column because the agitation could not be dissociated from the gas flow rate. When high gas velocities were tested, the transients of liquid saturation by hydrogen were not longer than that of the gas flow rate itself. However, for low gas velocities, it could be considered that this physical method gave a rough estimate. By measuring the dissolved hydrogen concentration before the beginning of the gas circulation, at a given time during agitation and at saturation, it was possible to calculate k_la. The values of k_la obtained by this physical method were about 30% larger than those estimated from the chemical method.

5.2.3. Correlations

The value of k_la found by the chemical method was quite consistent with that predicted by the correlations of [4] and [5]. At a gas velocity of $1.3 \cdot 10^{-2}$ m s^{-1}, the calculations gave respectively $3.8 \cdot 10^{-2}$ s^{-1} and $4.8 \cdot 10^{-2}$ s^{-1}, compared to $5 \cdot 10^{-2}$ s^{-1} obtained from the chemical method. These correlations were established with less efficient distributors than a porous plate, which could explain their underestimates.

5.3. Determination of deactivation function

No qualitative or quantitative piece of information about deactivation of Raney nickel in the adiponitrile hydrogenation was available. Hence only empirical laws could be proposed. They were supposed to depend only on time. The deactivation functions derived from: $-(d\Phi)/(dt) = k_d \Phi^n$, where k_d is the time constant for activity loss. (The term 'constant' was not appropriate because usually, k_d depended on different kinetic parameters and operating conditions.)

Several deactivation rate laws (order 0, 1 or n) were tested by means of the optimization software. The best accuracy between experimental runs and simulations was obtained assuming that the cata-

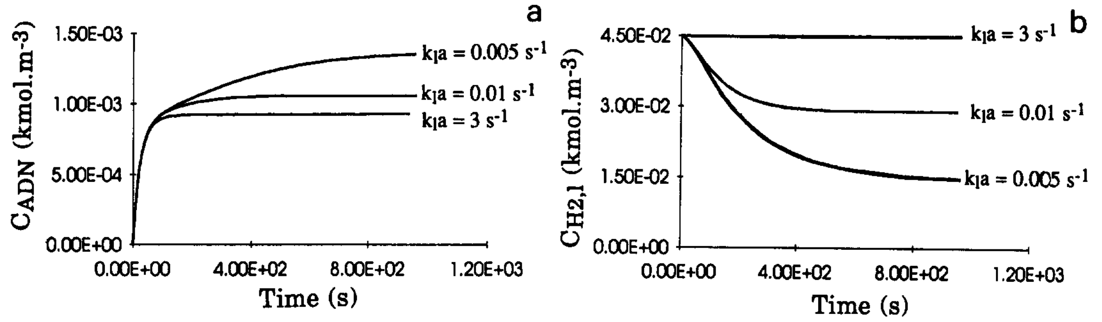


Fig. 5. (a) Effect of $k_l a$ on C_{ADN} and C_{ACN} for $F_{ADN,e}=0.7\cdot10^{-4}$ mol s^{-1}. (b) Effect of $k_l a$ on $C_{H2,l}$ for $F_{ADN,e}=0.7\cdot10^{-4}$ mol s^{-1}.

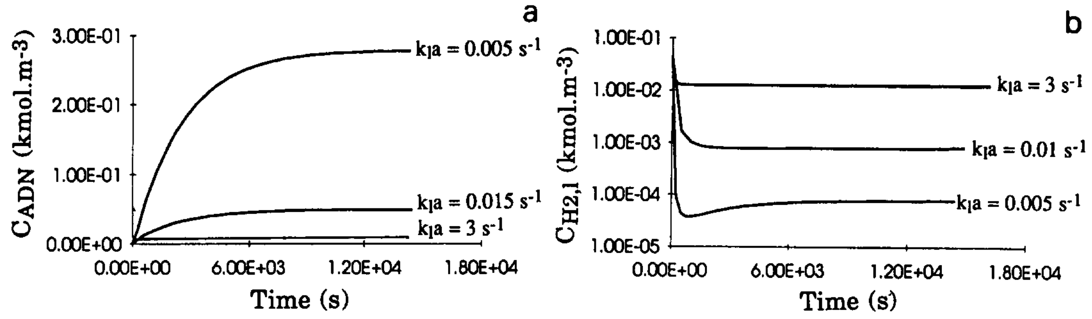


Fig. 6. (a) Effect of $k_l a$ on C_{ADN} and C_{ACN} for $F_{ADN,e}=3.5\cdot10^{-4}$ mol s^{-1}. (b) Effect of $k_l a$ on $C_{H2,l}$ for $F_{ADN,e}=3.5\cdot10^{-4}$ mol s^{-1}.

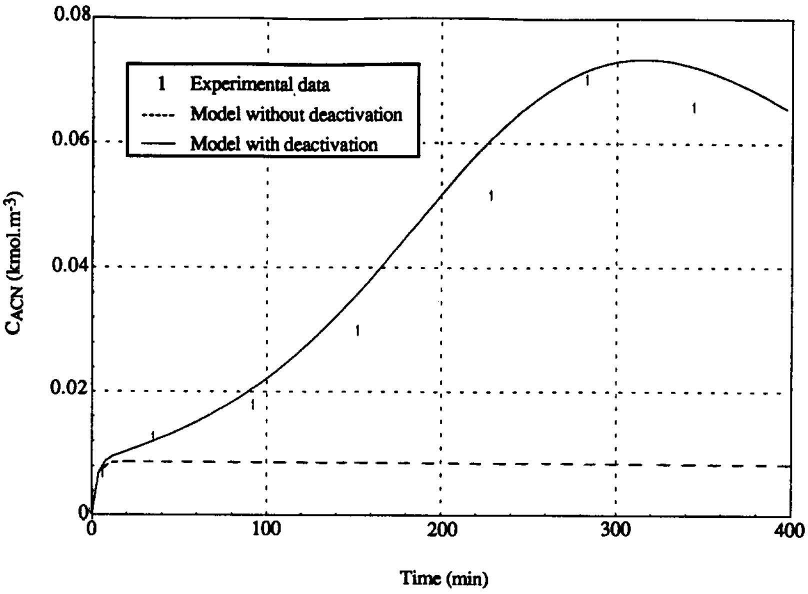


Fig. 7. (a) Effect of $k_l a$ on C_{ADN} and C_{ACN} for $F_{ADN,e}=3.5\cdot10^{-4}$ mol s^{-1}. (b) Effect of $k_l a$ on $C_{H2,l}$ for $F_{ADN,e}=3.5\cdot10^{-4}$ mol s^{-1}.

lyst activity decayed exponentially with time at constant temperature (Fig. 7).

The value of k_d was estimated for every experiment. It depended on the ratio (feed adiponitrile flow rate)/(catalyst loading). The higher this ratio was, the higher k_d was, hence the more important the deactivation was.

6. Conclusion

This work develops an example of comprehensive investigation of a three-phase catalytic process, involving a very broad experimental work, as heterogeneous catalytic kinetics, hydrodynamics, mass transfer and, finally, continuous reactor design, operation and control. The last part is of course, the most tedious and expensive one. That is the reason why such continuous experiments appear less often in literature. Yet they are indispensable for process development. It must be emphasized that continuous operation is not only the unique way to investigate deactivation but it is also often the best way to determine external mass transfer limitations in the actual reactor and reaction media.

7. Notations

$C_{H2,l}$	dissolved hydrogen concentration (kmol m^{-3}) (*: saturation)
C_i	concentration of species i (kmol m^{-3})
F_{ADN}	ADN flow rate (mol s^{-1})
k_d	time constant for activity loss (s^{-1})
k_la	volumetric gas–liquid mass transfer coefficient (s^{-1})
m	catalyst mass (kg)
Q	volumetric flow-rate (m^3 s^{-1})
r_j	rate of reaction j (kmol kg^{-1} s^{-1})
v_g	superficial gas velocity (m s^{-1})
V_R	reactor volume (m^3)
ϵ_g	gas holdup
Φ	deactivation function

Subscripts

e	at the reactor inlet
j	number of the reaction ($j=1$ for ADN → ACN and $j=2$ for ACN → HMD)

References

[1] P.M. Wilkinson and L.L. van Dierendonck, Chem. Eng. Sci., 45 (1990) 2309.

[2] C. Mathieu, E. Dietrich, H. Delmas and J. Jenck, Chem. Eng. Sci., 47 (1992) 2289.

[3] C. Joly-Vuillemin, D. Gavroy, G. Cordier, C. de Bellefon, H. Delmas, To be published in a special issue of Chem. Eng. Sci. from ISCRE 13, September 1994, Baltimore.

[4] K. Akita and F. Yoshida, Ind. Eng. Chem. Proc. Des. Dev., 12 (1973) 76.

[5] H. Hikita, A. Asai, K. Tanigawa, K. Segawa and M. Kitao, Chem. Eng. J., 22, (1981) 61.