MANIPULATION OF PRODUCT DISTRIBUTIONS VIA REVERSE FLOW OPERATION WITH SIDE FEEDING

Yogi W. Budhi
Research Group of Process Development of Design
Chemical Engineering Program Study, Faculty of Industrial Technology
Institut Teknologi Bandung
Labtek X, Jl. Ganesha 10, Bandung 40132
Phone: 022-2500989, Fax: 022-2501438
E-mail : Y.Wibisono@che.itb.ac.id

Abstract

A new concept of a reverse flow reactor with side feeding is studied for NH_3 oxidation to produce N_2, NO, and N_2O. In the conventional reverse flow operation, where the feeds are alternately introduced from either end of the reactor, the conversion always decreases when compared to steady state, once-through operation. The new concept of reverse flow operation with side feeding is therefore proposed to avoid the drop of conversion. The reactor behavior is simulated for three regimes (quasi-steady state, dynamic, sliding) with varying feed positions. The development of spatio-temporal patterns inside the reactor with side feeding shows completely different behavior compared to conventional reverse flow, leading to the possibility of conversion and selectivity manipulations.

Keywords: Ammonia oxidation, Conversion and selectivity improvement, Reverse flow reactor, Side feeding

Abstrak

Suatu konsep baru dari reaktor aliran balik dengan pengumpanan samping telah dipelajari dengan kasus oksidasi NH_3 untuk menghasilkan N_2, NO, dan N_2O. Pada operasi aliran balik konvensional dimana umpan secara bergantian dimasukkan dari ujung reaktor, konversi yang dihasilkan selalu menunjukkan penurunan ketika dibandingkan dengan keadaan tunaknya dalam satu tahap operasi. Konsep baru aliran balik dengan pengumpanan samping dimaksudkan untuk menghindari penurunan konversi. Perilaku reaktor disimulasi dalam 3 rejim aliran (quasi-steady state, dynamic, sliding) dengan memvariasikan posisi umpan. Pembentukkan pola spatio-temporal di dalam reaktor dengan pengumpanan samping menunjukkan perilaku yang berbeda dibanding aliran balik konvensional. Hal ini memungkinkan untuk memanipulasi konversi dan selektivitas.

Kata Kunci: Oksidasi Ammoniak, Pengumpanan Samping, Peningkatan Konversi dan Selektivitas, Reaktor aliran bolak-balik

1. Introduction

Periodically changing the flow direction through a reactor, known as Reverse Flow Operation (hereinafter referred to as RFO), is a typical example of forced unsteady state operation. It was proved beneficial for exothermic reactions from a viewpoint of energy saving (Matros, 1990 and 1996). However, this technique has not been widely applied for improvement of conversion or selectivity.

RFO with side feeding has already been considered to trap strongly adsorbing NH_3 species during the selective catalytic reduction of NO by NH_3 (Agar, 1988). Simulations showed that side stream NH_3 addition enables better mass trapping compared to addition from the ends and better control of axial adsorbate profiles (Synder, et al., 1998). A correlation was found between the reversal time to prevent the escape of the adsorbing species and the concentration of the non-adsorbing species. As a result, RFO with central introduction of adsorbing species could be more efficient than a conventional RFO (Falle, 1995). A RFO for NO reduction with central NH_3 introduction was also used for safety considerations in relation to ammonium salt formation on the catalyst (Noscov, et al, 1993 and Mearns, et al., 1984).

As the dynamics of RFO for manipulation of conversion and selectivity are much faster than their equivalents in the case of energy saving, it requires considerably more frequent flow reversals with a switching time in the same order of magnitude as the residence time is. This kind of operation induces a serious decrease of the conversion, which is mainly caused by an outflow of highly concentrated, unconverted reactant shortly after reversing the flow direction. This amount of gas actually has a shorter residence time and higher reactant concentration compared to the rest of the reactor's gas hold-up. To overcome the conversion decrease, a new concept of RFO with periodically lower feed concentration seems very promising (Budhi, et al, 2003).

Another option to improve the conversion in RFO is considered here by applying the concept of side feeding. The feed gas does not enter the reactor at $z = 0$ (forward flow) or $z = 1$ (backward flow) as usual, but at certain axial coordinates in between. The reactor outlet still flows out from the normal positions at $z = 0$ or $z = 1$, depending on the flow direction. Such an approach might be feasible to avoid the decrease of conversion because the gas with high reactant concentration that entered the reactor shortly before the flow direction is changed, now still may contact the catalyst before flowing out of the reactor. Moreover, the 'dead' gas volume in the reactor center, that exists if the switching time between flow reversals is smaller than the residence time, could possibly be avoided as well.

2. Fundamental

The research field of *dynamic reactor operation* is deliberately devoted to the developments of transient operation and control procedures for catalytic reactors with the objective to improve their performance. In transient reactor, one great challenge is to increase the reaction's conversion or selectivity through manipulation of the catalyst's surface coverage or heat storage capacity by suitable perturbations of the reactant inlet conditions or by dedicated flow reversals. From this research emerged the idea that under deliberately and artificially created unsteady state conditions, it is possible to increase the productivity, conversion, or selectivity, and to reduce the heat consumption of a catalytic process as a whole when compared to steady state performance. This issue is interesting from a viewpoint of *process intensification* (Stankiewicz and Moulijn, 2004).

Among the various options for transient operation, periodic operation offers the combined benefits of a permanent unsteady-state regime and a constant time-average regime. Periodically changing the flow direction through the reactor, better known as Reverse Flow Operation (hereinafter referred to as RFO), has been widely applied for exothermic reactions from a viewpoint of energy saving and for improvement of conversion or selectivity. The use of the reverse flow principle as transient operation procedure for a catalytic reactor becomes interesting by the combination of dynamic properties at a microscale (catalyst) and at a macroscale (reactor). It may produce more favourable concentration and temperature profiles for the catalytic process (Ferreira et al., 1999).

Former applications of reverse flow reactor were focused on the energy saving (Boreskov et al., 1982; Boreskov and Matros, 1983; Matros and Bunimovich, 1996; Matros, 1985, 1989; Froment, 1990; Neophytides and Froment, 1992). Further study on transient kinetic studies were performed to identify the relevant elementary reaction steps and to quantify the kinetic rate coefficients that are used in supporting modeling studies (Bobrova, Budhi, 2004). Basically, this might be achievable by a dedicated operation procedure for a fixed bed reactor with periodic flow reversal, aiming at selectivity improvements with respect to the desired product, or avoiding that the undesired products are detected at the reactor outlet.
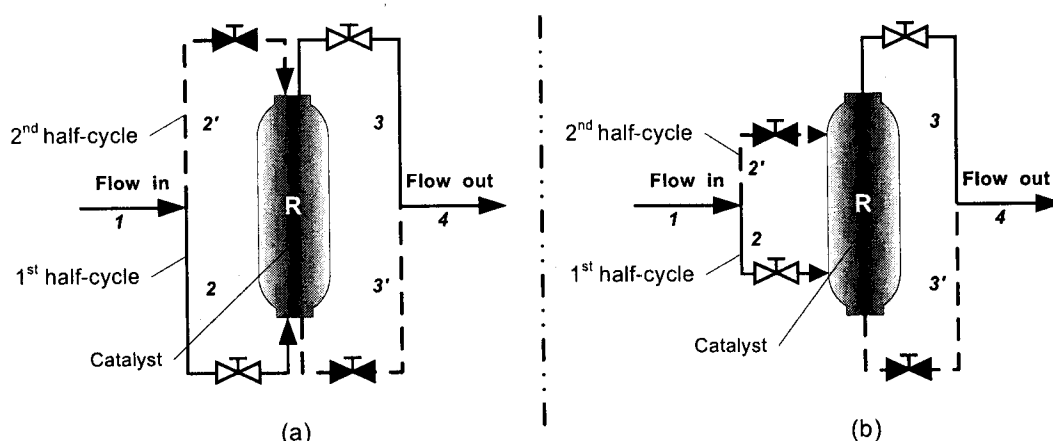
Figure 1. The principle diagram of reverse flow reactor: a. normal operation; b. with side feeding.
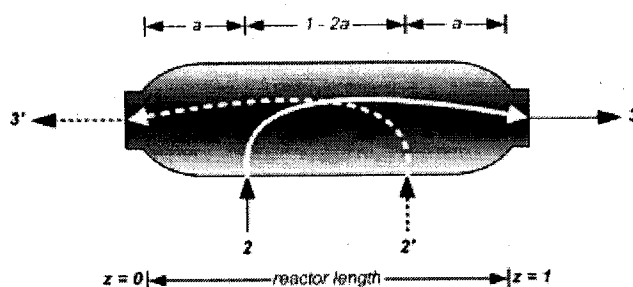

Figure 2. A scheme of the modeled reverse flow reactor with side feeding.

3. Methodology

A comparison between a conventional RFO and RFO with side feeding is shown in Fig. 1. Fig. 1a shows that during the 1st half of each cycle, the flow passes through 1-2-R-3-4 and during the 2nd half of each cycle, the flow passes through 1-2'-R-3'-4. Fig. 1b and Fig. 2 show the scheme with side feeding, defining the axial positions of the feeds and the distinct zones in the reactor. Feeds are positioned at axial coordinates $z = a$ and $z = 1 - a$ in terms of dimensionless reactor length. The regions $0 < z < a$ and $1 - a < z < 1$ are referred to as 'interrupted flow region', where the flow is alternately stopped or in one direction only. In the 'reverse flow region', $a < z < 1 - a$, the flow direction is periodically reversed.

A dynamic, pseudo-homogeneous, one-dimensional model of a fixed bed reactor was developed, assuming plug flow and isothermal conditions (Eqs. 1, 2, and 3). Axial dispersion was included only for reason of numerical stability. The axial dispersion coefficient was set to a value of 10^{-7} m^2/s, and it was verified that this value did not affect the simulation results. Pressure drop along the reactor bed was ignored. The complete model was solved numerically with the software package FlexPDE (PDE Solution Inc., 2001). The steady state situation for once-through operation was used as initial condition (Eq. 4), while conventional Danckwerts boundary conditions were applied for the gas phase equations (Eq. 5 for forward flow, Eq. 6 for backward flow). The model

Table 1. Model equations for the pseudo-homogeneous one-dimensional model, isothermal

$$\frac{\partial p_i}{\partial t} = -\frac{1}{\tau}\frac{\partial p_i}{\partial z} + D_{ef}\frac{\partial^2 p_i}{\partial z^2} + \frac{\sigma}{\varepsilon_b}\rho_b RT\sum r_k \quad (1)$$

$$p_i = p_i^{ss} \text{ and } \theta_i = \theta_i^{ss} \quad (4)$$

$$\frac{d\theta_j}{dt} = \sum r_k \quad (2)$$

$$\left.\frac{\partial p_i}{\partial z}\right|_{z=0} = 0, \ \left.\frac{\partial p_i}{\partial z}\right|_{z=a} = \frac{uL_r}{D_{ef}}\left(p_i^o - p_i\right) \ \left.\frac{\partial p_i}{\partial z}\right|_{z=1} = 0 \quad (5)$$

$$\theta^{ts} = 1 - \sum\theta_j^{ts} \text{ and } \theta^{hs} = 1 - \sum\theta_j^{hs} \quad (3)$$

$$\left.\frac{\partial p_i}{\partial z}\right|_{z=0} = 0, \ \left.\frac{\partial p_i}{\partial z}\right|_{z=L_r-a} = \frac{uL_r}{D_{ef}}\left(p_i^o - p_i\right) \ \left.\frac{\partial p_i}{\partial z}\right|_{z=1} = 0 \quad (6)$$

Table 2. Catalyst properties and operating conditions

Bed bulk density (kg/m_r^3)	1230	Inlet temperature T_{in} (K)	800
Void fraction (m_g^3/m_r^3)	0.45	Total pressure (atm)	1
Total number of sites (mol)	$6.85 \cdot 10^{-8}$	Superficial velocity u (cm/s)	0.135
Feed position a varied	0.1 – 0.4	NH_3 in feed (mol %)	1
Switching time t_s (s) varied	2 – 15	O_2 / NH_3 ratio in feed	2:1

equations are shown in Table 1.

Computer simulations were carried out on the basis of elementary steps with two different sites, notably top and hollow sites. The kinetic scheme for NH_3 oxidation over Pt/Al_2O_3 to produce N_2, NO, and N_2O was taken from literature (Rebrov, et al., 2003). Table 2 shows the operating conditions. Focus is on a comparison of conversion and selectivity, obtained in a RFO with both normal feeding and side feeding. Three kinds of regime are considered, i.e. quasi-steady state, dynamic, and sliding regimes.

4. Results and Discussion

Fig. 3 a2, b2, and c2, provides typical examples of the simulated NH_3 partial pressure at a = 0.1 for three different regimes, represented by different switching times. The base case (Fig. 3 a1,

b1, c1) represents results at similar conditions, with the feed position at the ends of reactor ($z = 0$ and $z = 1$). After reversing the flow direction in the quasi-steady state regime (Fig. 3 a1), the outlet concentration profile of the base case reaches the steady state value as shown by the horizontal part of the profiles.

When side feeding is applied (Fig. 3 a2), the concentration profiles in between the inlet points are also able to reach the steady state, while the concentration profiles in the interrupted flow region stay in the unsteady state. Shifting the feed position toward the reactor's center causes a higher concentration of NH_3 in the interrupted flow region if flown through, and a lower concentration due to the continuing reaction if not flown through. Although this concentration is lower, it remains lower only for a short while after the flow direction
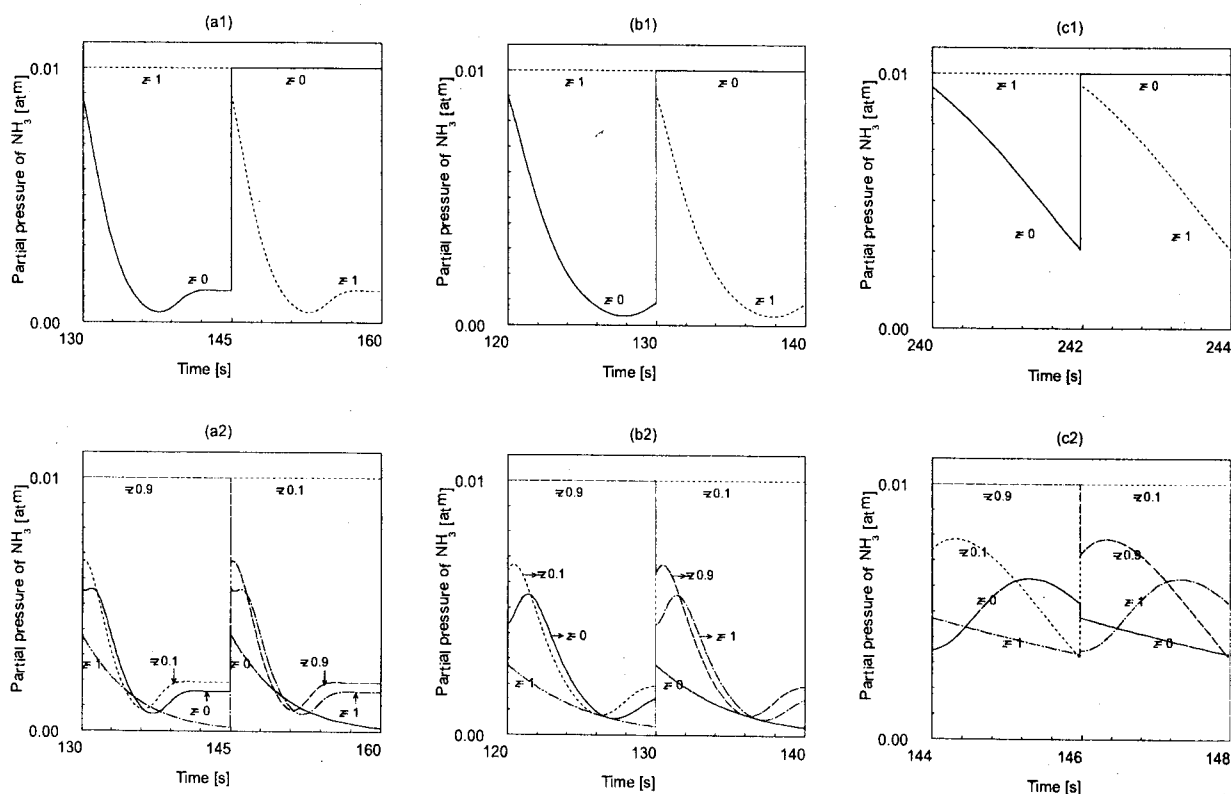

Figure 3. Gas phase NH_3 profiles as function of time at discrete positions in the reactor during one cycle. Operating conditions as mentioned in Table 2: (a1). quasi-steady state (t_s = 15 s), base case; (b1). dynamic (t_s = 10 s), base case; (c1). sliding (t_s = 2 s), base case; (a2). quasi-steady state (t_s = 15 s), a = 0.1; (b2). dynamic (t_s = 10 s), a = 0.1; (c2). sliding (t_s = 2 s), a = 0.1.

is reversed and the interrupted flow region is flown through. The behavior in the dynamic regime looks similar as in the quasi-steady state, but just before reaching the steady state, the reactor is perturbed by reversing the flow direction (Fig. 3 b1). With side feeding, the interrupted flow region concentration is a little higher than in the quasi-steady state due to faster switching (Fig. 3 b2).

In the sliding regime, the concentration profiles look completely different. All profiles remain in the unsteady state and depend strongly on the ratio of switching time over residence time. When this ratio approaches unity, the behavior looks similar as in the dynamic regime. For $a = 0.1$, the concentration levels in the sliding regime are higher than in the other regimes, but the opposite holds for a-values over 0.3.

Fig. 4 shows the conversion of NH_3 and the selectivities toward N_2, NO, and N_2O as function of the feed position at different switching times, which reflect the various operation regimes. In general, there are two effects that have an influence on the conversion when moving the feed positions to the reactor center: a). the volume of the interrupted flow region increases, which causes a higher conversion of more residing gas, and less outflow of unreacted gas shortly after a flow reversal; b).the volume of the rest of the reactor decreases, which lowers the conversion obtained in this part. In the quasi-steady state, the conversion of NH_3 decreases non-monotonously when the feed positions are shifted to the reactor center. This behavior is rather complicated, possibly caused by an interaction of the effects a) and b) mentioned before.
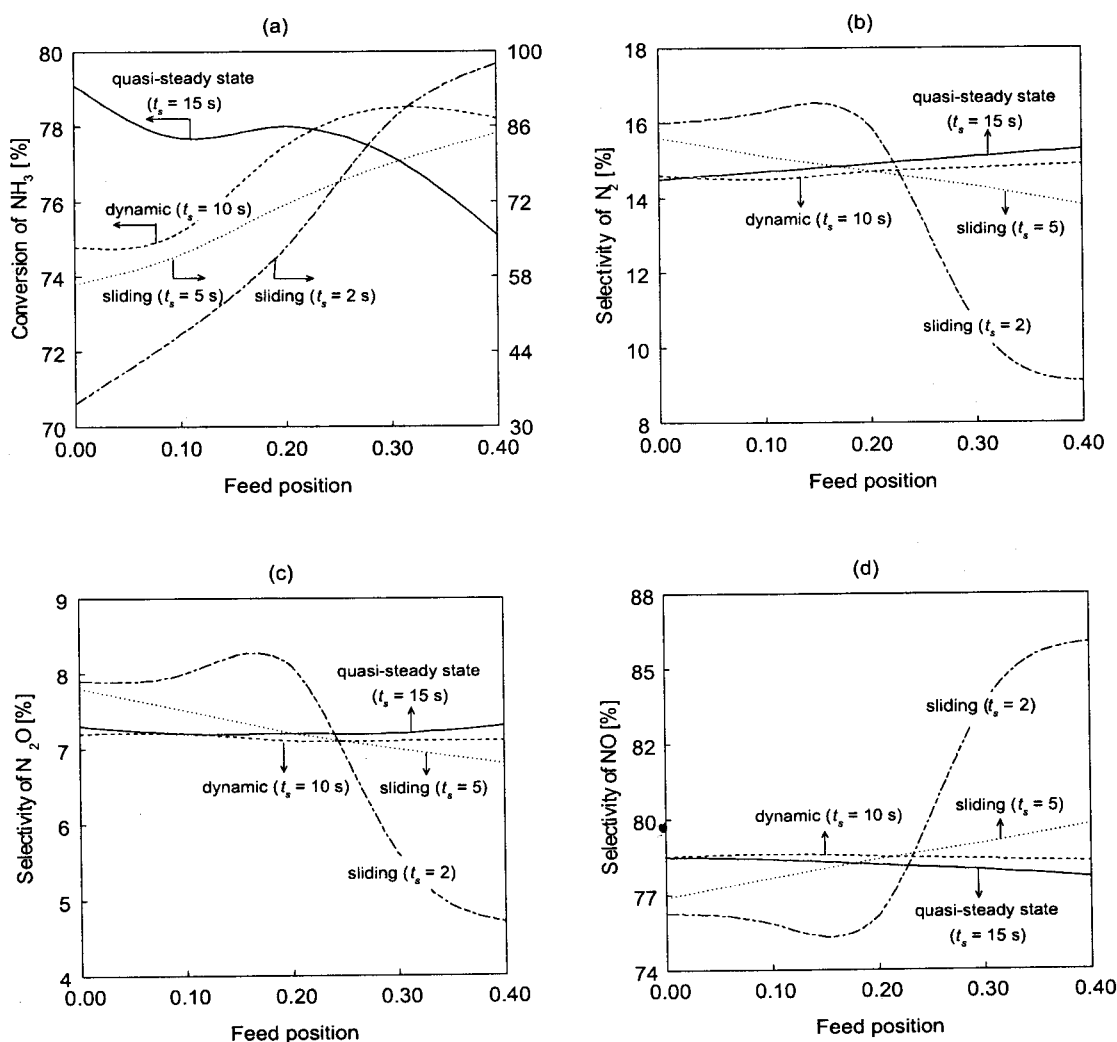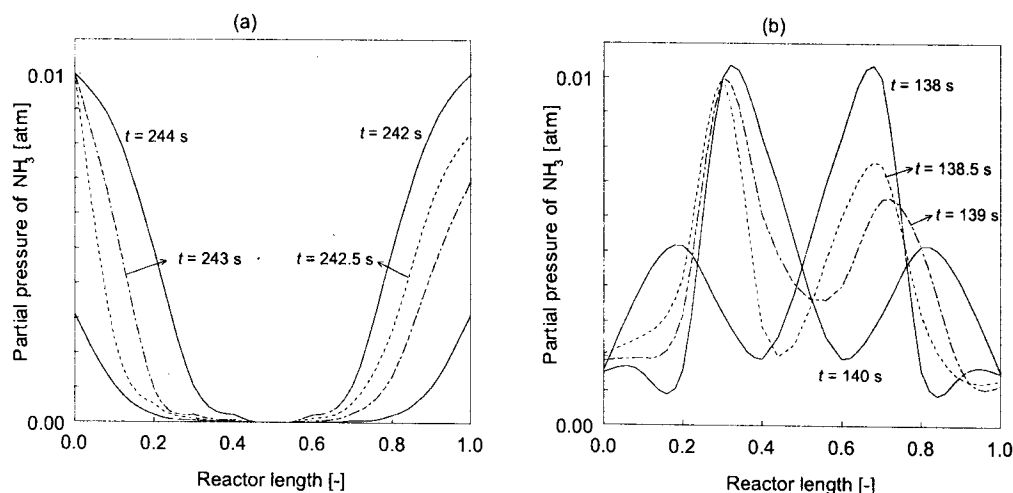

Figure 4. Conversion of NH_3 and selectivity of N_2, N_2O, and NO as function of the feed positions in term of dimensionless reactor length. Operating conditions as mentioned in Table 2.

Figure 5. Gas phase NH₃ profiles along the axial dimensionless reactor axis at discrete time during the period of one half-cycle in the sliding regime. Switching time is 2 s. Other operating conditions as mentioned in Table 2: (a). base case, (b). side feeding; $a = 0.3$.

The behavior in the dynamic regime looks similar as in the quasi-steady state, but the general trend is now increasing. The influence of the feed position in quasi-steady and dynamic regimes is not impressing, contrary to the effects in the sliding regime. Here, two different switching times of 5 and 2 s were applied. In both cases, the conversion of NH_3 shows a large increase when the feed positions are shifted to the reactor center. The effect is most pronounced if the switching time is shorter, causing the gas to reside longer in the interrupted flow region. Shifting the feed positions to the reactor center may avoid the occurrence of a dead gas volume in the center. If a dead gas volume does exist, its band becomes narrower, which has a negligible influence compared to the effect of a longer residence time in the interrupted flow region.

RFO with side feeding also affects the selectivity of the products. Although the conversion level itself has an influence on the selectivity, the differences in product distributions result from RFO as shown by a comparison to the steady state at constant conversion (Budhi, et al., 2003). Fig. 4 b, c, and d show the effect of side feeding on the selectivity. The selectivity of N_2 increases slightly in the quasi-steady and dynamic regimes if the feed positions shift to the reactor center. It decreases, however, significantly in sliding regime, especially at high flow reversal frequency. The selectivity of N_2O shows similar behavior as N_2 in the sliding regime. In the other regimes, the feed position hardly has an influence. The selectivity of NO also shows minor changes in the quasi-steady and dynamic regimes if the feed positions shift to the reactor center, but the NO selectivity increases considerably in the sliding regime.

Fig. 5 shows how the NH_3 profiles along the dimensionless reactor axis develop in time at four discrete time values during one half-cycle in the sliding regime. Normal RFO is shown in Fig. 5a and RFO with side feeding at $a = 0.3$ in Fig. 5b. At the end of the half-cycle, the flow direction is reversed by feeding at the other inlet position. The profile existing at the start of every half-cycle is the mirror image of the profile developed at the end of every half-cycle. With normal feeds, a zero NH_3 concentration level appears in the reactor center, which is caused by the full conversion of the trapped gas in the central reactor part. It exhibits the presence of the dead gas volume, which is an ineffective use of the catalyst. This dead gas volume can be flushed regularly with fresh feed gas after some cycles of RFO, leading to a conversion increase (Budhi, et al., 2003). By side feeding, the presence of the dead gas volume can be avoided permanently if the feeds are positioned at suitable points. This may lead to an effective catalyst use in the sliding regime.

5. Conclusions

A reverse flow reactor with side feeding was modeled and simulated for quasi-steady, dynamic, and sliding regimes for particular case of NH_3 oxidation. The concept shows a promising way to affect the distribution of products as well as the conversion in case of a sliding regime. Also, the dead gas volume can be permanently avoided.

Notation

D_{ef} : axial dispersion coefficient, $m^2 s^{-1}$
L_r : dimensionless reactor length, $m\, m^{-1}$
p : partial pressure of gas, atm
R : ideal gas constant, $1\, atm\, mol^{-1}\, K^{-1}$
r : reaction rate, s^{-1}
t : time, s
t_s : switching time, s
T : temperature, K
u : superficial velocity, $m\, s^{-1}$
z : dimensionless axial position

Greek letters

ε_b : bed porosity, $m^3_{gas}\, m^{-3}_{reactor}$
ρ_b : bed density, $kg_{cat}\, m^{-3}_{reactor}$
θ_j : surface coverage
σ : catalyst mol site, $mol\, kg^{-1}_{cat}$
τ : residence time, s

Superscripts

hs : hollow site
ts : top site

Subscripts

b : bed
k : elementary step, $k = 1, 2, 3, ..., 13$
r : reactor
s : switching

References

[1]. Matros, Yu. Sh., (1990), "Performance of catalytic processes under unsteady conditions", *Chemical Engineering Science*, 45, 2097-2102.

[2]. Matros, Yu. Sh., Bunimovich, G. A., (1996), "Reverse flow operation in fixed bed catalytic reactors", *Catalysis Review–Science and Engineering*, 38, 1, 1-68.

[3]. Agar, D.W., Ruppel, W., (1988), "Extended reactor concept for dynamic deNOx design", *Chemical Engineering Science*, 43, 2073-2078.

[4]. Synder, J.D., Subramaniam, B., (1998), "Numerical simulation of a reverse-flow NOx-SCR reactor with side-stream ammonia addition", *Chemical Engineering Science*, 53, 727-734.

[5] Falle, S.A.E.G., Kallrath, J., Brockmuller, A., Schreieck, A., Giddings, J.R., Agar, D.W., Watzenberger, O., (1995), "The dynamics of reverse flow chromagraphic reactors with side stream feed", *Chemical Engineering Communication*, 135, 185-211.

[6]. Noskov, A.S., Bobrova, L.N., Matros, Yu. Sh., (1993), "Reverse-process for NOx-off gases decontamination", *Catalysis Today*, 17, 293-300.

[7]. Budhi, Y.W., Hoebink, J.H.B.J., Schouten, J.C., (2003), "Simulation of reverse flow operation for manipulation of catalyst surface coverage in the selective oxidation of ammonia", *Proceedings of the 4th International Conference on Unsteady-State Processes in Catalysis*, Montreal, Canada.

[8]. Moulijn, J.A., Stankiewicz, A., Grievink, J., Górak, A., (2004), "Process intensification and process systems engineering: A friendly symbiosis", *Computers & Chemical Engineering*, 32, 3-11..

[9]. Ferreira, R.Q., Costa, C.A., Masetti, S., (1999), "Reverse-flow reactor for a selective oxidation process", *Chemical Engineering Science*, 54, 4615-4627.

[10]. Boreskov, G.K., Matros, Yu.Sh., (1983), "Flow reversal of reaction mixture in a fixed catalyst bed - a way to increase the efficiency of chemical processes", *Applied Catalysis*, 5, 337-343.

[11]. Matros, Yu.Sh., Bunimovich, G.A., Strots, V.O., Mirosh, E.A., (1999), "Reversed flow converter for emission control after automotive engines", *Chemical Engineering Science*, 54, 2889-2898.

[12]. Matros, Yu.Sh., Noskov, A.S., Chumachenko, V.A., (1993), "Progress in reverse-process application to catalytic incineration problems", *Chemical Engineering and Processing*, 32, 89-98.

[13]. Vanden Bussche, K.M., Neophytides, S.N., Zolotarskii, I.A., Froment, G.F., (1993), "Modelling and simulation of the reversed flow operation of a fixed-bed reactor for methanol synthesis", *Chemical Engineering Science*, 48, 3335-3345.

[14]. Froment, G.F., (1986), "The kinetics of catalytic processes: Importance in reactor simulation and design", *Applied Catalysis*, 22, 3-20.

[15]. PDE Solutions Inc., (2001), *"FlexPDE 3. User Guide and Reference Manual"*.

[16]. Rebrov, E.V., de Croon, M.H.J.M., Schouten, J.C., (2003), "Development of the kinetic model of platinum catalyzed ammonia oxidation in a microreactor", *Chemical Engineering Journal*, 90, 61-76.

[17]. Mearns, A.M., Ofosu-Asiedu, J.K., (1984), "Ammonium nitrate formation in low concentration mixtures of oxides of nitrogen and ammonia", *Chemical Technology and Biotechnology*, 34a, 350-354.