



# Reactor performance enhancement under periodic operation for the ethanol dehydration over $\gamma$ -alumina, a reaction with a stop-effect

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## Abstract

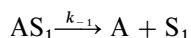
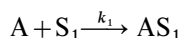
The possibility of enhancing reactor performance under forced cycling of the inlet feed was investigated for the ethanol to ethene dehydration reaction over  $\gamma$ -alumina. This reaction presents a stop-effect, i.e. a drastic increase of the reaction rate for a stepwise decrease in the inlet concentration of ethanol (Koubek et al., 1980a, b; Moravek and Kraus, 1984). This phenomenon is due to an educt inhibition, leading to the existence of an optimal inlet concentration of ethanol under steady-state conditions. Periodic operation can be used advantageously to increase the performance of the ethene production up to values higher than the maximal steady-state value. The maximum enhancement is achieved for short non-symmetric periods, with the major part of the cycle under inert gas. It was shown by simulations that for an integral reactor the parameters of the cycle have to be adjusted to the residence time. Finally the two-sites model developed for the stop-effect (Golay et al., 1997, 1999) is able to predict qualitatively the influence of all the cycle parameters. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Ethanol dehydration; Periodic operation; Stop-effect; Performance enhancement; Modelling

## 1. Introduction

The ethanol to ethene dehydration on  $\gamma$ -alumina presents a stop-effect behaviour (Fig. 1), i.e. a drastic increase of the reaction rate when the feed concentration of a reactant is switched to zero. This temporary increase of the reaction rate under transient conditions was first reported by Koubek et al. (1980a, b) for the catalytic dehydration of alcohols and the deamination of amines on aluminas, zeolites or more generally, on amphoteric metal oxide catalysts. In previous studies ethanol dehydration was investigated by simultaneous measurements of the gas-phase composition by gas chromatography and of the concentration of adsorbed species on the catalyst surface by in situ infrared spectroscopy (Golay et al., 1997, 1998, 1999). The results were described by a model [Eqs. (1)–(6)], considering the existence of acid and basic sites,  $S_1$  and  $S_2$ , respectively, on the catalyst

surface. Ethanol can adsorb either strongly on acid sites [Eqs. (1) and (2)] or weakly on basic sites [Eq. (3)], and a free basic site is required for the ethene formation [Eq. (4)]. At steady state the reaction rate is low due to the low concentration of free  $S_2$  sites. The desorption of the weakly adsorbed species under inert gas liberates the elimination reaction sites, and causes the observed increase of the reaction rate. The exhaustion of the reacting species is responsible for the decrease of ethene formation in the second part of the transient. The second ethene formation step [Eq. (5)] describes the second rate enhancement observed at the end of the transient, which requires an exponential activity distribution of the rate constant to be depicted. Diethylether formation can be described, for simplicity, by a quasi-homogeneous reaction term [Eq. (6)]. The adsorbed intermediates  $AS_1$ ,  $AS_2$  were identified as surface-bound ethoxides.

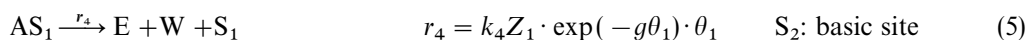
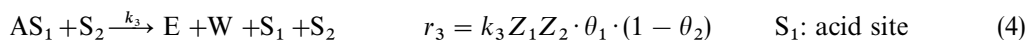
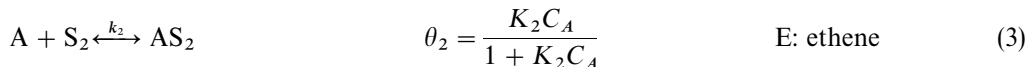


$$r_1 = k_1 Z_1 \cdot C_A \cdot (1 - \theta_1) \quad \text{A: ethanol} \quad (1)$$

$$r_{-1} = k_{-1} Z_1 \cdot \theta_1 \quad \text{D: diethylether} \quad (2)$$

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Eqs. (1)–(4) have already been applied by Thullie and Renken (Thullie and Renken, 1991) to simulate the expected reactor performance under forced concentration oscillations in a differential reactor. Their theoretical calculations, which assume an identical concentration of acid and basic sites, show that under relaxed steady-state conditions and with an optimum cycle split, the rate enhancement factor increases monotonically beyond the maximal rate obtained under optimum steady-state conditions. The relaxed steady-state operation requires the use of very short periods hardly obtainable from a practical point of view. Furthermore the  $\gamma$ -alumina does not contain an identical amount of acid and basic sites for ethanol dehydration (Golay et al., 1997). Therefore preliminary simulations were carried out, with the complete model and parameters derived from transients (Golay et al., 1999), which showed that an enhancement of the reactor performance under periodic operation was also possible in an integral reactor.

The objectives of this work were to study the use of periodic operation in a real tubular reactor for a reaction which presents an educt inhibition, and to verify that the enhancement predicted by simulation was possible under realistic conditions. The average ethene performance was hence measured at a reaction temperature of 180°C as a function of the three main variables that arise in

periodic operation (defined on Fig. 2): cycle period ( $t_p$ ), cycle split ( $s$ ) and mean inlet concentration ( $\bar{C}_{A,0}$ ).

## 2. Experimental

The apparatus, catalyst and gases employed have been previously described in detail (Golay et al., 1997). The flow-apparatus consisted of two feed sections converging to a four-way valve, a fixed-bed integral reactor and a gas chromatograph. Residence time distribution experiments showed that the fixed bed behaves almost like a plug-flow reactor, and it was consequently described by a tanks-in-series model. The time delay between the four-way valve and the gas chromatograph is about 5 s and hence can be neglected.

The carrier gas was argon (>99.99%, Carbagas, Lausanne, Switzerland) and the ethanol (>99.8%, No. 02860, Fluka Chemie AG, Buchs, Switzerland) feed was provided by a temperature-controlled bubble column fed by argon.

As catalyst,  $\gamma$ -alumina (Type Al-3982, Engelhard De Meern B.V., De Meern, The Netherlands) was used in this study. The BET specific area is 162 m<sup>2</sup>/g and the average pores diameter 7.4 nm. 510 mg of catalyst were used.

The experiments were carried out at a temperature of 180°C, a pressure of 140 kPa, and a total flow-rate of 200 ml (NTP)/min.

## 3. Results and discussion

### 3.1. Steady-state kinetics

The influence of the inlet ethanol concentration on the steady-state ethene formation is shown on Fig. 3. It can be seen that an optimum steady-state exists at low inlet concentration, due to the educt inhibition. This optimal concentration was found to be 0.013 mol/m<sup>3</sup>. On one hand, decreasing the concentration diminishes the inhibition due to the sorption on the basic sites and increases the ethene formation. On the other hand the surface coverage of the acid sites also decreases, decreasing the ethene formation. The optimal concentration is the concentration that maximises the product between the

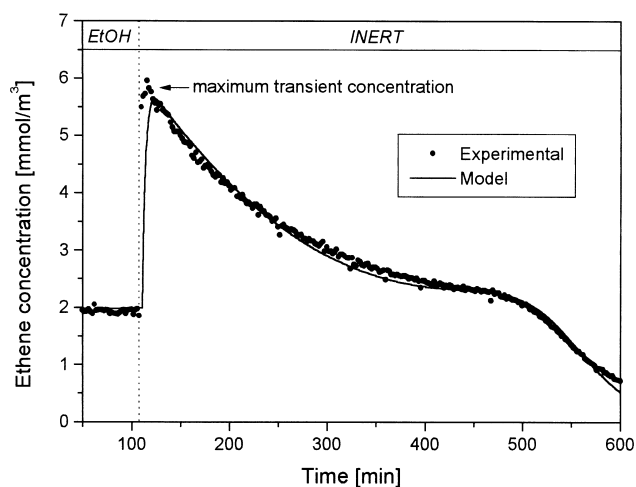


Fig. 1. Typical transient experiment.  $T_R = 180^\circ\text{C}$ ;  $C_{A,0} = 0.26 \text{ mol/m}^3$ ;  $Q = 200 \text{ ml (NTP)/min}$ ;  $m_{\text{cat}} = 510 \text{ mg}$ .

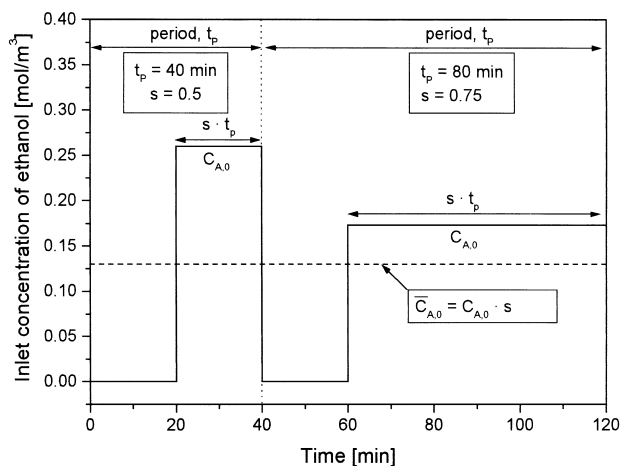


Fig. 2. Definition of the cycling variables: cycle period,  $t_p$ ; cycle split,  $s$ ; mean inlet concentration,  $\bar{C}_{A,0}$ .

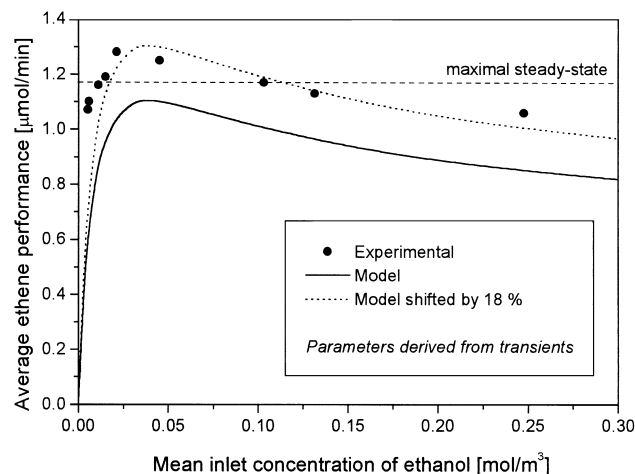


Fig. 4. Influence of the mean inlet concentration of ethanol on the average ethene performance under periodic conditions. The model parameters are those derived from transients (Golay et al., 1998b).  $T_R = 180^\circ\text{C}$ ;  $Q = 200$  ml (NTP)/min;  $m_{\text{cat}} = 510$  mg;  $t_p = 20$  min;  $s = 0.5$ .

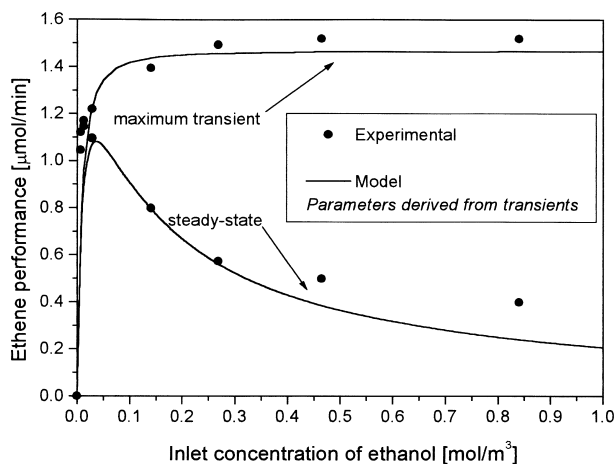


Fig. 3. Influence of the inlet concentration of ethanol on the steady-state and maximum transient ethene performance. The model parameters are those derived from transients (Golay et al., 1999).  $T_R = 180^\circ\text{C}$ ;  $Q = 200$  ml (NTP)/min;  $m_{\text{cat}} = 510$  mg.

average concentration of ethoxides adsorbed on the acid sites and the average concentration of empty basic sites over the complete catalytic bed.

It can also be seen in Fig. 3 that the maximum ethene concentration reached during the stop-effect (defined in Fig. 1) can be up to 20% higher than the optimum steady-state value. This confirms that under transient conditions a catalyst surface state can be achieved, which could never have been obtained under steady-state conditions.

### 3.2. Kinetics under periodic conditions

#### 3.2.1. Influence of the inlet concentration of ethanol

The influence of the mean inlet concentration of ethanol on the average ethene performance has been

measured for a cycle period of 20 min and a cycle split of 0.5, i.e. symmetric periods. Similarly to the steady-state results a maximum is measured (Fig. 4) for a mean inlet concentration of  $0.021 \text{ mol}/\text{m}^3$ . The shift to a higher concentration is mainly due to a lower averaged coverage of the basic sites under periodic conditions compared to the steady-state values, for the same mean inlet concentration of ethanol. The maximal measured steady-state performance is reported in Fig. 4 for comparison with the periodic results. An enhancement of about 10% is achieved under periodic conditions with this set of period and split values.

The experimental results were simulated with the two-sites model [Eqs. (1)–(6)]. As the cycle periods used in this work are always shorter than 300 min, the second rate enhancement is not observed under periodic conditions. The second step for ethene formation [Eq. (5)] hence can be neglected. The differential equations of the mass balance for the gas phase and the surface species were solved simultaneously as a function of time and axial position in the reactor, using the Gear variable step integration algorithm (Simusolv, 1990). The model parameters are those derived from transients (Golay et al., 1999). It can be seen in Fig. 4 that the general shape of the computed curve corresponds to the measurements. However the description is not quantitative: the simulated curve is consistently 18% lower than the measured one. This shift of the computed curve is mainly due to the impossibility of determining  $k_1$  by transients, due to the lack of sensitivity for this parameter. Moreover it can be seen from Fig. 1 that the two-sites model does not exactly describe the rapid increase of the ethene concentration directly after the stop and underestimates the maximum concentration reached under transient

conditions. These imperfections have a strong influence on the modelling of the periodic experiments, due to the short periods which were used. They result from an underestimated rate of liberation of the basic sites after the stop in the ethanol feed. This underestimation is due to simplifications made by the two-sites model. For example, diethylether formation is described by a quasi-homogeneous reaction term, whereas it occurs by reaction of surface species. The consumption of  $AS_2$  to form diethylether after the stop should hence be taken into account. Also an activity distribution of the basic sites probably exists, which is not considered. Independent experiments are being currently carried out in our laboratory to determine the model parameters for these phenomena.

Since the model parameters derived from transients can only depict qualitatively the influence of the cycle parameters, the periodic data were directly simulated. The model parameters were optimised to describe the ethene concentration at the reactor outlet using the Nelder–Mead search algorithm and the likelihood function as the objective function (Simusoly, 1990). A new set of parameters was thus determined, and it can be seen in Fig. 5 that a general good agreement is achieved between experiments and simulations. The decrease in the ethene concentration when the ethanol feed is started and which is due to the coverage of the basic sites is underestimated, probably for similar reasons to those discussed for the modelling of the transients.

The influence of the other cycle parameters on the reactor performance was then studied. The reactant feed was set to the value leading to optimal steady-state conditions, a mean inlet concentration of ethanol of  $0.013 \text{ mol/m}^3$ , to compare performances for an identical reactant input. The cycle period and cycle split were varied to determine their optimal values.

### 3.2.2. Influence of the cycle period

The influence of the cycle period with a cycle split of 0.5 is shown on Fig. 6. When the period is decreased, the ethene performance increases monotonously and then reaches a plateau. For periods under 80 min, the average performance is higher than the maximal steady-state performance. The maximum enhancement is about 3%.

When the period is increased, the ethene production under inert gas becomes less important compared to that under ethanol, inducing a decrease of the average ethene performance. For very long periods, this performance tends to a quasi-steady-state value, where the transient production of ethene can be neglected. The quasi-steady state value is estimated to be half of the steady-state value obtained with an inlet concentration two times higher than the mean inlet concentration. It was found to be  $0.6\% \mu\text{mol/min}$ . For small periods, the ethanol feed is too short to maintain a sufficient mean coverage of the ethene precursor,  $AS_1$ . This effect compensates the increase of the average ethene concentration during the inert part of the cycle, explaining therefore the existence of the plateau observed.

### 3.2.3. Influence of the cycle split

The influence of the cycle split on the average ethene performance, for a cycle period of 20 min, is shown in Fig. 7. When the split is decreased, the ethene performance increases regularly. A 10% increase over the maximal steady-state performance is achieved with a cycle split of 0.05. Decreasing the split implicates the use of a higher inlet concentration of ethanol (Fig. 2), lowering the ethene concentration measured under ethanol (Fig. 3). However, both the relative transient contribution and the relative duration of the cycle period under inert gas increase. These two effects lead to the augmentation of the average ethene concentration over the complete

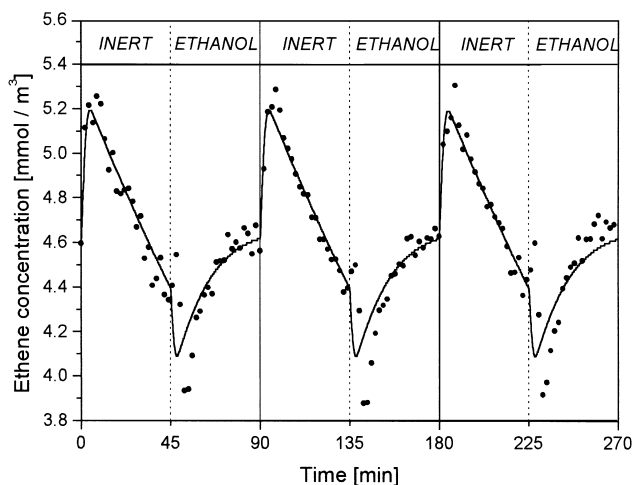


Fig. 5. Typical example of comparison between the experimental and simulated kinetics under periodic conditions.  $T_R = 180^\circ\text{C}$ ;  $Q = 200 \text{ ml (NTP)/min}$ ;  $m_{\text{cat}} = 510 \text{ mg}$ ;  $\bar{C}_{A,0} = 0.013 \text{ mol/m}^3$ ;  $t_p = 90 \text{ min}$ ;  $s = 0.5$ .

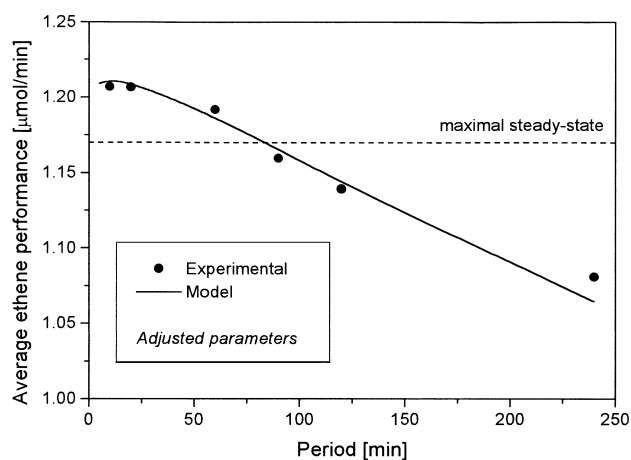


Fig. 6. Influence of the cycle period on the average ethene performance under periodic conditions.  $T_R = 180^\circ\text{C}$ ;  $Q = 200 \text{ ml (NTP)/min}$ ;  $m_{\text{cat}} = 510 \text{ mg}$ ;  $\bar{C}_{A,0} = 0.013 \text{ mol/m}^3$ ;  $s = 0.5$ .

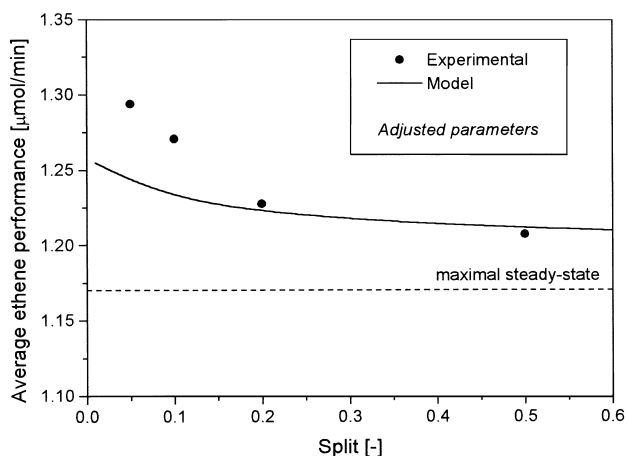


Fig. 7. Influence of the cycle split on the average ethene performance under periodic conditions.  $T_R = 180^\circ\text{C}$ ;  $Q = 200$  ml (NTP)/min;  $m_{\text{cat}} = 510$  mg;  $\bar{C}_{A,0} = 0.013$  mol/m<sup>3</sup>;  $t_p = 20$  min.

cycle, which is mainly due to the high speeds of adsorption and desorption on the basic sites,  $S_2$ . If the adsorption step on these sites was not instantaneous, the maximum transient increase would be lower, and so would be the average ethene formation (Thullie and Renken, 1991).

#### 3.2.4. Influence of the residence time on the performance under periodic conditions

The modified residence time, defined as the ratio between the catalyst mass and the total flow rate, that was used is low and gives rise to a differential behaviour of the reactor for ethene formation. Therefore simulations were carried out to determine the influence of the residence time on reactor performance. These verified that enhancements can also be achieved in an integral reactor. In Fig. 8 the average ethene performance is reported as a function of the cycle period for four reduced residence times. In an integral reactor (reduced residence times of 4 and 8 and 20), the maximum is broader than in a differential reactor (reduced residence time of 0.25) and displaced to higher cycle periods.

For a high inlet concentration of ethanol (0.20 mol/m<sup>3</sup>), the use of a differential reactor is not advantageous. An optimum residence time exists which maximises the reactor performance. The existence of such an optimum is consistent with the influence of the inlet concentration of ethanol (Fig. 3) and is due to the existence of a pronounced axial profile of concentration along the catalyst bed.

## 4. Conclusions

The performance for the ethene production in a real tubular reactor can be increased by the use of periodic

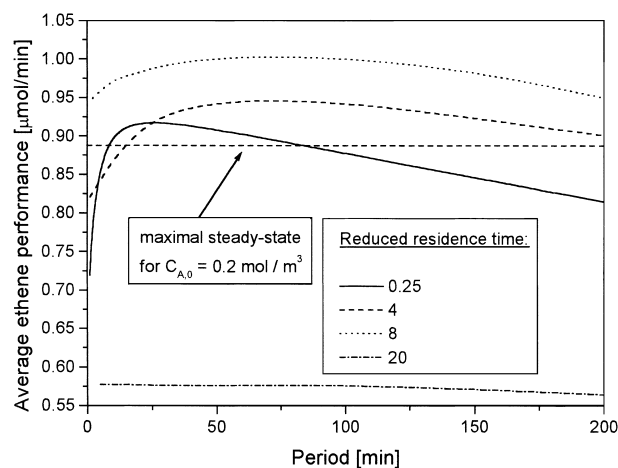


Fig. 8. Influence of the residence time on the optimum cycle period. The model parameters are those derived from transients (Golay et al., 1998a).

operation. By varying the inlet concentration of ethanol, the cycle period or the cycle split, it is always possible to find conditions where the performance is higher than the maximum steady-state value.

The enhancement is higher when short non-symmetric periods are used, with a longer part of the cycle under inert gas. This is due to the short time required to adsorb enough ethanol on the surface, which can react in the second part of the cycle. In an integral reactor, the optimal cycle parameters have to be adapted to the residence time.

The two-sites model can predict qualitatively the influence of all the cycle parameters, but requires further modifications for a quantitative description.

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## Notation

A	ethanol
BET	Brunauer, Emmet, Teller
C	gas phase concentration, mol/m <sup>3</sup>
D	diethylether
E	ethylene
k	rate constant, various units
K	equilibrium constant, m <sup>3</sup> /mol
m	catalyst mass, mg
NTP	normal conditions of temperature and pressure, 0°C, 1.013 × 10 <sup>5</sup> Pa
Q	flow rate, ml (NTP)/min

s	cycle split, dimensionless
S	catalytic site
T	temperature
W	water
Z	concentration of surface sites, mol/kg

#### Greek letters

$\theta$	surface coverage, dimensionless
$\tau$	cycle period, min
$\phi$	ratio between the concentration of $S_1$ and the concentration of $S_2$ , dimensionless

#### Subscripts

0	at reactor inlet
1	acid site
2	basic site
A	ethanol
cat	catalyst
R	reactor

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