

# Optimal dynamical processes in tubular reactor with deactivation of multi-run moving catalyst

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## Abstract

The dynamic unsteady-state reactor process in a cocurrent tubular reactor with single-run reagents (continuous phase) and with multi-run catalyst (dispersed phase) has been investigated. For the temperature-dependent catalyst deactivation the reactor process has been considered in which after optimal number  $B$  of catalyst residences in the reactor the whole amount of catalyst leaves the system; then the fresh catalyst is directed to the reactor and the next  $B$ -runs cycle of the optimal process starts. The optimization problem has been formulated in which a maximum of an average (for one cycle) process profit flux is achieved by a best choice of number  $B$  of catalyst residences in the reactor and best choice of temperature profiles along tubular reactor for each catalyst run,  $b = 1, \dots, B$ , respectively. The set of parallel-consecutive reactions,  $A + B \rightarrow R$  and  $R + B \rightarrow S$ , with desired product  $R$  has been taken into account. The algorithms of maximum principle have been used for optimization. Optimization procedure allows for finding an optimal number of catalyst runs  $B$  for which an average process profit flux reaches a maximum for a concrete value of fresh catalyst price  $\lambda$ . Optimal value of  $B$  increases with  $\lambda$ . A shape of optimal temperature profile constitutes the effect of compromise between the overall production rate of desired reagent  $R$  (production rate in the first reaction minus disappearance rate in the second one) and the necessary savings of catalyst. The optimal solutions show that the most important influence on the optimal temperature profile is due to the need of catalyst saving; low temperatures save catalyst during its initial runs. Moreover, the optimal temperature profile is independent of fresh catalyst price  $\lambda$ . If optimal temperature profile for  $B$ -run reaction process is known, then, to obtain optimal profile for  $(B-r)$ -run process, it is enough to cut the initial part of optimal profile corresponding to the first  $r$  runs.

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## 1. Introduction

An optimization problem, which regularly appears for various catalytic reactors, is that of optimal temperature control. Examples of catalytic reactors where the problem is important were presented by us at Second and Third International Symposium on Catalysis in Multiphase Reactors [1,2]. A frequently encountered reaction system involves a set of parallel-consecutive reactions (1) and (2), with a desired product  $R$ , which undergo in a tubular reactor with moving deactivating catalyst (granular solid). For a temperature

dependent and concentration independent catalyst decay, deactivation rate is described by Eq. (3), where the activity  $a$  is defined as the ratio of reaction rate in presence of given catalyst to the rate in presence of fresh catalyst [3] and  $T(t)$  for  $0 \leq t \leq t_k$  describes the temperature profile along reactor. The net profit flux accompanying reactor process can be expressed as difference between gross return determined by economic value of desired product  $R$  and total process cost. The optimal temperature profile has to maximize the net profit flux.



$$\frac{da(t)}{dt} = -k_{d0} \exp(-E_d/RT(t)) a(t) \quad (3)$$

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### Nomenclature

$a$	catalyst activity
$a_f$	fresh catalyst activity
$B$	number of catalyst residences in reactor
$b$	current number of catalyst residences in reactor
$c_i$	concentration of reactant $i$ (mol/l)
$F$	performance index defined by Eq. (12)
$K_c$	fixed cost (\$/min)
$L$	mass flux of reagents in reactor (kg/min)
$M_R$	molar mass of desired product $R$
$P$	net profit flux $P$ (\$/min)
$r$	number of the first initial runs of catalyst
$S$	catalyst mass flux in reactor (kg/min)
$T$	temperature (K)
$t_k$	common residence time of reagents and catalyst in reactor during its single run along reactor (min)
$\beta$	dimensionless catalyst flux, Eq. (14)
$\lambda$	dimensionless unit price of fresh catalyst, Eq. (13)
$\mu_f$	fresh catalyst price (\$/kg)
$\mu_R$	price of desired product $R$ (\$/kg)
$\rho_L$	density of reacting mixture
$\rho_S$	catalyst density

The papers quoted above refer to steady-state reaction processes with single-run reagents, where the changes are along the length of reactor (no recycling), and with single-run catalyst or its partial recycling. It should be underlined that for processes with partial recycling of catalyst, the existence of fresh catalyst flux  $S_f$  allows for these processes to be in a steady-state. For dynamic unsteady-state processes, that are the subject matter of this paper, the fresh catalyst flux  $S_f$  does not exist—compare Fig. 1 and Fig. 3. Therefore, for dynamic unsteady-state processes it is required that the whole amount of catalyst is exchanged after an optimal number  $B$  of catalyst residences occurs in the reactor.

The both papers, [1,2], underline that the most important influence on the optimal temperature profile is associated with necessity of saving the catalyst.

$$R = S_r/S_f \quad (4)$$

In the paper [2], which refers to the process presented in Fig. 1, catalyst recycle ratio has been defined by Eq. (4). The rates of reactions have been described by expressions

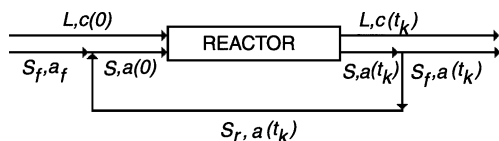


Fig. 1. Cocurrent tubular reactor with catalyst recycle.

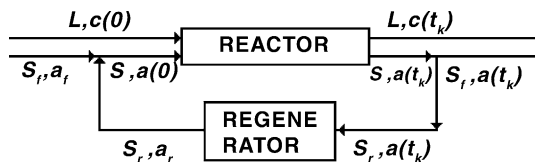


Fig. 2. System of cocurrent tubular reactor-catalyst regenerator.

containing (temperature dependent) reaction rate constants, concentrations of reagents, catalyst activity, as well as catalyst concentration in the reacting suspension and a measure of the slip between reagents and solid catalyst particles. The optimal solutions show that a shape of the optimal temperature profile depends on mutual relations between activation energies of reactions and catalyst deactivation. It has been proved that the optimal temperature profile is a result of the compromise between the overall production rates of desired reagent  $R$  (production rate in the first reaction minus disappearance rate in the second one), necessity of saving of reagents residence time (reactor volume) and necessity of saving catalyst. The most important role of the optimal temperature profile is associated with its influence on saving of the catalyst: When catalyst recycle ratio increases (mean number of catalyst particles residing in reactor increases) optimal temperatures save the catalyst, as the optimal profile is shifted in direction of lower temperatures. The same is observed when catalyst slip increases; in this case the optimal profile is shifted in direction of lower temperatures. When reactor unit volume price decreases, catalyst residence time increases, whereas optimal temperature profile is shifted to lower temperatures.

The paper [1] refers to the system of cocurrent tubular reactor-catalyst regenerator presented in Fig. 2 (it is note worthy that both the existence of catalyst regenerator as well as existence of fresh catalyst flux  $S_f$  admits steady-state processes). The optimal solutions show that an increase of the unit cost of catalyst regeneration or an increase of the catalyst recycle ratio cause such optimal temperatures in reactor which save the catalyst, as the optimal temperature profiles are shifted towards lower temperatures.

The papers [1,2] refer to typically steady-state processes whereas the optimization of dynamic unsteady-state reactor processes with (still) single-run reagents but with multi-run catalyst is a task of this paper. In the processes considered here, after optimal number  $B$  of catalyst residences in the reactor the whole amount of catalyst leaves the system; then the fresh catalyst is directed to the reactor and the next cycle of the optimal process starts, Fig. 3. Our purpose here is to outline the optimization procedure that uses an average (for

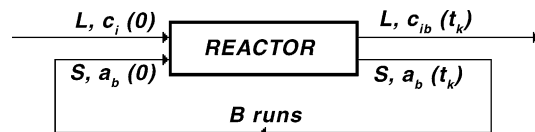


Fig. 3. Dynamic unsteady-state tubular reactor (the system investigated in the present paper).

one cycle) profit flux of the process as a performance index, which is maximized subject to the temperature profile as a process control.

However, before any optimization development the reader should be warned that that the analysis in the present paper does not refer to the most typical scheme of the catalytic contacting represented by the fixed bed reactor, thus no similarities with fixed bed reactors optimization are expected. Our work refers to an unsteady-state reactor with a moving deactivating catalyst, presented in Fig. 3. The total mass of the catalyst in this reactor is set as the product of the catalyst residence time  $t_c$  and the catalyst flux,  $S$ . Similarly as the reactors shown in Figs. 1 and 2 (that refer to our previous analyses in papers [1] and [2]) also the reactor presented in Fig. 3 (the object of our investigation here) belongs to the class of reactors with moving deactivating catalyst. However, while each of the reactors in Figs. 1 and 2 can achieve the steady-state mode in any stable reaction process (sustained by a finite, fixed flow of the solid phase,  $S_f$ ), the reactor of Fig. 3 can only work as an unsteady-state system. An additional common property of the reactors presented on all three figures is that each element of the continuous phase of reagents resides in the reactor only once (single-run phase). On the other hand, the moving deactivating catalyst (solid phase flow,  $S$ ) can reside in the reactor many times, and, therefore, the sets of states (paths) followed by the moving deactivating catalyst are different in each run. This causes an essential difference between the processes in Figs. 1 and 2, and the process in Fig. 3.; processes undergoing in reactors of Figs. 1 and 2 are usually steady in time whereas the ones in reactor in Fig. 3 are always the unsteady-state. This also influences the mode of the optimization analysis which differs substantially in our paper from that in refs [1] and [2].

Regarding the process of Fig. 1 its stationarity follows from the finite flux of the fresh catalyst. This stationarity is preserved in spite of diverse number of residences of various catalyst grains in the reactor. The number of the residences of a definite grain in the reactor lies between zero and an infinity; hence the activity of a definite catalyst grain in the reactor is between the activity of the fresh catalyst and zero. On the other hand, an average number of the catalyst grain residences increases with the value of the catalyst recycle index. Accordingly, an average activity of the catalyst grain in the reactor decreases with the recycle index,  $R$ .

Regarding the process of Fig. 2 its stationarity, in the general case, is the result of both factors: a finite flux of the fresh catalyst,  $S_f$ , and the regenerator. Here, the residence path of catalyst grains is such that each grain that resides in the regenerator more than once is subjected a regeneration process in the regenerator, between each subsequent residence in the reactor. In practice such a process scheme is accomplished in the catalytic cracking of the crude oil.

For a “frozen” regeneration of the catalyst, the regenerator in Fig. 2 would become a container of the recycled catalyst with the unchanged catalyst grains flowing through it. This process would be identical with the process in the reactor in

Fig. 1 subject the assumption of the piston catalyst flow. Still the considered process would remain a steady-state process. On the other hand, for the vanishing feed flux in the process in Fig. 2 (at the inlet and the outlet) the process would work at a steady-state provided that catalyst grain regeneration is possible to a fixed activity, independent of the regeneration number. This is usually not a case because the decaying catalyst acquires (as the result of subsequent regenerations) lower and lower activities [5]. Therefore the process in the reactor–regenerator system without the fresh catalyst feed is an unsteady-state process (similarly like the process in Fig. 3). In this process, after the expiration of a period of its working time (the result of optimization) the whole amount of the catalyst in the system (i.e. the sum of the catalyst amount in the reactor and regenerator) is removed from the system and replaced by the fresh catalyst.

Also, in the process optimized here (Fig. 3) the whole amount of the catalyst is exchanged after an optimal number of the catalyst residences  $B$  (optimal number of “runs”). The optimum value of  $B$  is therefore an important outcome of the optimization.

Now we shall focus on the process in Fig. 3 exclusively. We designate:  $c_i(0)$  is concentration of reactant  $i$  in inlet reagent flux, independent of catalyst run index  $b$ ;  $t_k$  residence time of reagents in reactor and also catalyst residence time in reactor during its single run through reactor;  $c_{ib}(t_k)$  concentration of reactant  $i$  in outlet reagents flux during catalyst run  $b$ , where  $b = 1, \dots, B$ ;  $a_b(0)$  inlet catalyst activity during catalyst run  $b$ , where  $b = 1, \dots, B$ , satisfying relationship

$$a_b(0) = a_{b-1}(t_k) \quad (5)$$

with initial condition  $a_1(0) = a_f$ , where  $a_f = 1$  is a fresh catalyst activity;  $a_b(t_k)$  outlet catalyst activity during catalyst run  $b$ , where  $b = 1, \dots, B$ .

## 2. Mathematical model of catalyst deactivation and chemical reactions

For the considered dynamic multi-run processes Eq. (3) is applied in the form

$$\frac{da_b(t)}{dt} = -k_{d0} \exp\left(\frac{-E_d}{RT_b}(t)\right) a_b(t) \quad (6)$$

that contains explicitly run index  $b$ . Eq. (6) is valid for  $b = 1, \dots, B$  and  $0 \leq t \leq t_k$ .

The catalytic reactions (1) and (2) are described by Eqs. (7)–(10) valid for  $b = 1, \dots, B$  and  $0 \leq t \leq t_k$ . The reaction rate constants  $k_1$  and  $k_2$  satisfy Arrhenius equation with activation energies  $E_1$  and  $E_2$ , respectively.

$$\frac{dc_{Ab}(t)}{dt} = -k_1(T_b(t)) a_b c_{Ab} c_{Bb} \quad (7)$$

$$\frac{dc_{Bb}(t)}{dt} = -k_1(T_b(t)) a_b c_{Ab} c_{Bb} - k_2(T_b(t)) a_b c_{Bb} c_{Rb} \quad (8)$$

$$\frac{dc_{Rb}(t)}{dt} = k_1(T_b(t))a_b c_{Ab} c_{Bb} - k_2(T_b(t))a_b c_{Bb} c_{Rb} \quad (9)$$

$$\frac{dc_{Sb}(t)}{dt} = k_2(T_b(t))a_b c_{Bb} c_{Rb} \quad (10)$$

### 3. Process profit flux

The net profit flux  $P$  accompanying reactor process can be expressed as difference between gross return determined by economic value of desired product  $R$  and process cost consisting cost of fresh catalyst and fixed cost  $K_c$ . Note that the cost flux of fresh catalyst appears only in the catalyst run's  $b = 1$ , thus an average rather than instantaneous profit flux  $P$  should be considered. If the inlet reacting mixture does not contain desired reagent  $R$  and the catalyst leaving the system (after the last run  $B$ ) is worthless one, the average net profit flux  $P$  referred to one process cycle can be expressed as

$$P = \frac{1}{B} \sum_{b=1}^B \frac{L}{\rho_L} c_{Rb}(t_k) M_R \mu_R - \frac{1}{B} S \mu_f - K_c, \quad (11)$$

where the first term on the right-hand side of Eq. (11) describes an average (for  $B$ -runs cycle) economic value of desired reagent  $R$  with its molar mass  $M_R$  and price  $\mu_R$ . This reagent is contained in the volumetric flux  $L/\rho_L$  of reagent mixture with concentration  $c_{Rb}(t_k)$  in output flux (catalyst run  $b$ ). The second term on the right-hand side of Eq. (11) describes the average for  $B$ -runs cycle economic value of fresh catalyst (fresh catalyst flux appears only in the run  $b = 1$ ).

Eq. (11) can be transformed into the form

$$F = \frac{P + K_c}{(L/\rho_L) M_R \mu_R} = \frac{1}{B} \sum_{b=1}^B c_{Rb}(t_k) - \frac{1}{B} \lambda \beta, \quad (12)$$

where:

$$\lambda = \frac{(\mu_f \rho_s)}{(\mu_R M_R)} \quad (13)$$

$$\beta = \frac{(S/\rho_s)}{(L/\rho_L)} \quad (14)$$

As the cost  $K_c$  and expression  $(L/\rho_L) M_R \mu_R$  are given constants, for the purpose of optimization, performance index  $P$  can be replaced by performance index  $F$  described by Eq. (12) or Eq. (15)—consider stoichiometric Eqs. (1) and (2) and kinetic Eq. (9):

$$F = \frac{1}{B} \sum_{b=1}^B \int_0^{t_k} \{k_1[T_b(t)]a_b(t)c_{Ab}(t)c_{Bb}(t) - k_1[T_b(t)]a_b(t)c_{Bb}(t)c_{Rb}(t)\} dt - \frac{1}{B} \lambda \beta \quad (15)$$

Performance index  $F$  has to be maximized by optimal choice of number of catalyst runs (number of catalyst resi-

dences in reactor) during one optimal cycle and optimal temperature profile along reactor for every catalyst residence in reactor,  $b = 1, \dots, B$ . Of course, when performance index  $F$  is maximized, the dynamic (state) Eqs. (6) and (7)–(10) have to be satisfied. The production of  $R$  is calculated as the component of the process profit.

### 4. Results of numerical computations

For optimization calculation the discrete optimization algorithm with a constant Hamiltonian [4] worked out by the authors of this paper, is applied.

The optimization calculations were performed for the same data of reaction kinetics and catalyst deactivation kinetics as those in our earlier papers [1,2]:  $E_1 = 67$  kJ/mol,  $K_{10} = 5 \times 10^3$  l<sup>2</sup>/(mol min m<sup>2</sup>),  $E_2 = 125$  kJ/mol,  $K_{20} = 3 \times 10^{10}$  l<sup>2</sup>/(mol min m<sup>2</sup>)  $E_d = 105$  kJ/mol,  $K_{do} = 4 \times 10^{15}$  min<sup>-1</sup>,  $c_A(0) = c_B(0) = 1$  mol/l,  $c_R(0) = c_s(0) = 0$   $T_* = 335$  K and  $T^* = 355$  K (where  $T_*$  and  $T^*$  describe minimal and maximal allowable temperature, respectively), as well as  $\beta = 0.1$   $t_k = 1$  min and various values of dimensionless unit price of fresh catalyst  $\lambda$ . The results obtained are presented in Figs. 4–6. For more details see ref. [6]

Optimization procedure allows for finding an optimal number of catalyst runs  $B$  for which performance index  $F$  reaches maximum for concrete value of fresh catalyst price  $\lambda$ . Fig. 4 shows that optimal value of  $B$  increases with  $\lambda$ . For  $\lambda = 0$ , e.g. for the case when fresh catalyst price is very low and can be approximated by zero, the maximum of profit flux  $P$  represented by the maximum of performance index  $F$  is reached for  $B = 1$ . This means that, in the optimal process, the catalyst has to leave the system after only one residence in the reactor. For more expensive fresh catalyst e.g.  $\lambda = 0.2$ , the maximum of performance index  $F$  is reached for  $B = 2$ . This means that in the optimal process the catalyst in reactor has to leave the system after two residences. And so on: for  $\lambda = 0.4$  the optimal number  $B$  of catalyst residences in the reactor is  $B = 3$ , whereas for  $\lambda = 0.6$   $B = 4$

A shape of optimal temperature profile constitutes the effect of compromise between the overall production rate of desired reagent  $R$  (production rate in the first reaction mi-

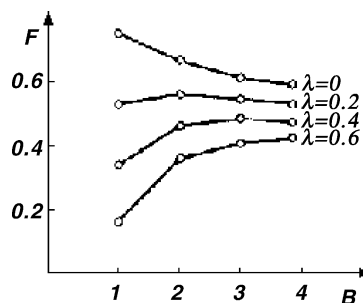


Fig. 4. Optimal performance index vs. total number of catalyst runs, for various prices of fresh catalyst.

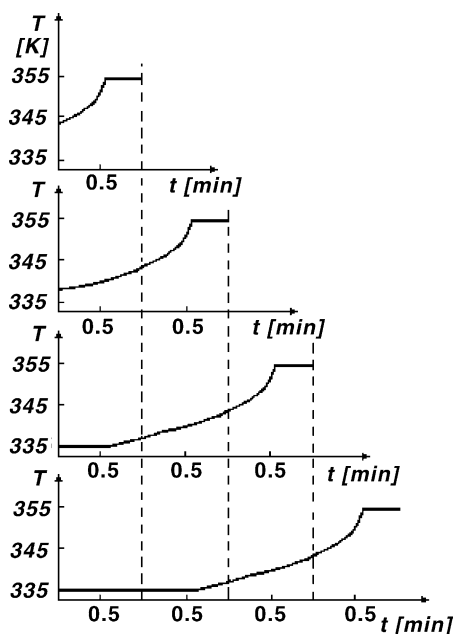


Fig. 5. Optimal temperature profiles for successive runs in 1-, 2-, 3- and 4-run processes.

nus disappearance rate in the second one) and the necessary savings of catalyst. The results presented in Figs 5 and 6 show that the most important role of the optimal temperature profile is due to its influence on catalyst saving; low temperatures save catalyst during its initial runs. To show that optimal temperature strategies save catalyst during its initial runs it is enough to compare optimal temperature profiles along the length of reactor for the first catalyst run, for various optimal

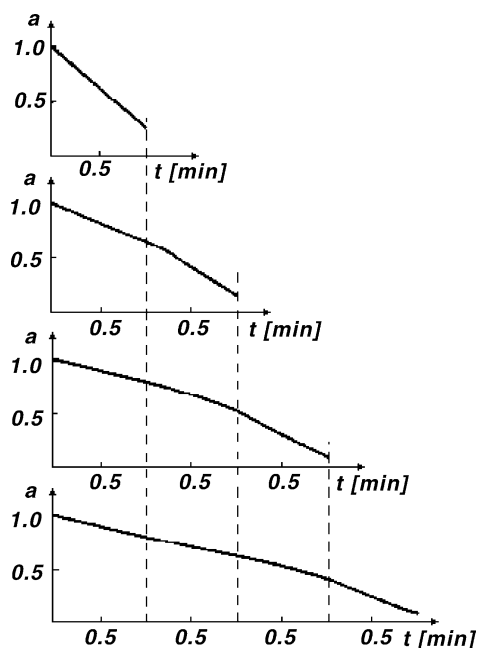


Fig. 6. Optimal catalyst activity trajectories for successive runs in 1-, 2-, 3- and 4-run processes.

number of catalyst residences in reactor  $B$ . For  $B = 1$  the curve  $a(t)$  is rapidly going down. When  $B$  increases the curve  $a(t)$  becomes more and more flat.

Moreover, an optimal temperature profile is independent of fresh catalyst price  $\lambda$  (Fig. 5, valid for various  $\lambda$ ). This is because the functional properties of costs are unchanged with  $\lambda$ .

If optimal temperature profile for  $B$ -run reaction process is known, then, to obtain an optimal profile for  $(B-r)$ -run process, it is enough to cut the initial part of optimal profile corresponding to the first  $r$  runs.

## 5. Concluding remarks

For a dynamic unsteady-state reactor processes in a cocurrent tubular reactor with single-run reagents (continuous phase) and with multi-run catalyst (dispersed phase) the optimization problem has been formulated. In such processes after optimal number  $B$  of catalyst residences in the reactor the whole amount of catalyst leaves the system; then the fresh catalyst is directed to the reactor and the next  $B$ -runs cycle of the optimal process starts. In this optimization problem a maximum of an average (for one cycle) process profit flux is achieved by a best choice of number  $B$  of catalyst residences in the reactor and best choice of temperature profiles along tubular reactor, for each catalyst run,  $b = 1, \dots, B$ , respectively. The set of parallel-consecutive reactions,  $A + B \rightarrow R$  and  $R + B \rightarrow S$ , with desired product  $R$  has been taken into account. A relatively unknown discrete optimization algorithm of maximum principle type has been used for optimization [4,6].

It has been shown that an optimal number of catalyst runs  $B$  for which an average process profit flux reaches a maximum exists for every concrete value of fresh catalyst price  $\lambda$ . Optimal value of  $B$  increases with  $\lambda$ .

A shape of optimal temperature profile constitutes the effect of compromise between the overall production rate of desired reagent  $R$  and the necessary savings of catalyst. The optimal solutions show that the most important influence on the optimal temperature profile is due to the need of catalyst saving; low temperatures save catalyst during its initial runs. Moreover, an optimal temperature profile is independent of fresh catalyst price  $\lambda$ . If optimal temperature profile for  $B$ -run reaction process is known, then, to obtain optimal profile for  $(B-r)$ -run process, it is enough to cut the initial part of optimal profile corresponding to the first  $r$  runs.

The described above situation with cutting of the initial part of optimal temperature profile is known for non-catalytic parallel reactions, leading to desired reagent  $R$  and undesired reagent  $Q$ , respectively. In this case a shape of optimal temperature profile constitutes the effect of compromise between the production rate of desired reagent  $R$  and production rate of undesired reagent  $Q$ . In our catalytic problem undesired direction of process is the one which leads

to catalyst deactivation. For non-catalytic parallel reactions problem undesired direction of process is that one which leads to undesired product  $Q$ . A suitable explanation of both cases is as follows: whenever a production of undesired product  $Q$  takes place, valuable reagents are consumed, hence they cannot be used in production of the desired product  $R$ . This effect is common in both catalytic and non-catalytic systems.

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