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Modeling local/periodic temperature variation in catalytic reactions

Jasper Stolte*, Jochem Vissers, Ton Backx and Okko Bosgra

Abstract— **This paper introduces a dynamic simulation model for investigation of local and transient effects in catalytic reaction systems. More specifically, the model allows inspection of the effects of supplying thermal energy directly to the catalytic particles in stead of applying energy to the whole reactor volume.**

With simulation results it is shown that for a certain type of catalytic reaction system the obtainable yield of product and the selectivity of the reaction toward that product can be significantly increased when thermal energy is supplied directly to the catalyst. It is also shown that the results can be improved even further by supplying thermal energy periodically in stead of continuously.

I. INTRODUCTION

Chemical processes are often operated in steady-state. In the modeling and design of these processes it is commonly assumed that the reactor is ideally mixed. The environmental variables like temperature, pressure and concentration are then assumed to be homogeneous throughout the whole system. Control of the process is a matter of keeping the environmental variables as close as possible to the precomputed optimal steady state conditions. Inhomogeneities, both spatial and temporal, are regarded undesirable for reasons such as safety or adherence to strict product specifications.

From a control engineering point of view the steady state and the perfectly mixed assumptions are strong limitations. Relaxing these constraints allows extra degrees of freedom for process design. When understood and controlled properly the extra freedom could be used to improve the process at hand (process intensification), or even to develop completely new process control methods which introduce more flexibility into plant operation. On-line control over product specifications, and fast on/off switching of the reactions are only the most obvious applications.

A direction of research where inhomogeneous spatial conditions can already be found is the field of microwave enhanced, or microwave assisted chemistry [1]–[3]. In this field of research a part of the energy supplied to a reaction system is in the form of microwave irradiation. Significant gains in product yield, selectivity and/or reaction times have been reported [4]. There is an ongoing debate in literature on whether the effects observed with microwave irradiation are caused by temperature effects only, or whether 'microwave effects' may be responsible. Currently, consensus is growing that temperature inhomogeneity is likely to be the primary cause [3].

A field where inhomogeneities in time are found is the field of periodic control. Studies suggest that it is possible to advantageously use unsteady state control, by deliberately applying periodic trajectories [5]–[8]. Some examples of applications with this technology have been reported [9].

Most of the works referred to above have been undertaken by chemists and chemical engineers, who traditionally use quasi-steady-state modeling techniques or finite volume techniques. In the control systems literature, the results do include chemical dynamics, most importantly dealing with stability of chemical reactors through feedback [10], [11]. In this paper the approach will be essentially open-loop, selecting favorable input trajectories for temperature in time and space. The unidirectional reaction scheme considered guarantees overall system stability.

To our knowledge, no successful effort has been undertaken to create dynamic models for chemical reactors that can handle both local and transient phenomena without resorting to computationally expensive finite volume methods. This paper presents a reactor model which is capable of handling both local and transient phenomena. Simulations with the model in sections III and IV show significant improvement in process characteristics for the test case reaction system when energy is supplied locally and/or periodically, and offer an explanation why this is observed.

In section II the two-compartment model developed to attack the problem is elucidated. A test case reaction system is also introduced there. Section III shows results of local steady state simulations of the test case reaction in the two-compartment model. In section IV the simulation is extended to local and transient control of the test case reaction system.

II. METHOD

This section elucidates the developed simulation model and test case reaction system used in this paper. The starting point from which the model is developed is the (ideally mixed) continuous stirred tank reactor (CSTR). A schematic of a CSTR with temperature control is shown in figure 1.

The CSTR with temperature as an input has only the concentrations of the reactants C_i in $\left[\text{mol } m^{-3}\right]$ as states. For a reaction system of N reaction steps, each state is governed by differential equation (1):

$$\frac{dC_i}{dt} = \frac{\phi}{V_r}(C_{i0} - C_i) + \sum_{j=1}^{N} p_{ij} \qquad (1)$$

where ϕ is the input flow in $[m^3\ s^{-1}]$, V_r is the volume of the reactor in $[m^3]$, p_{ij} is the rate of production of species i by

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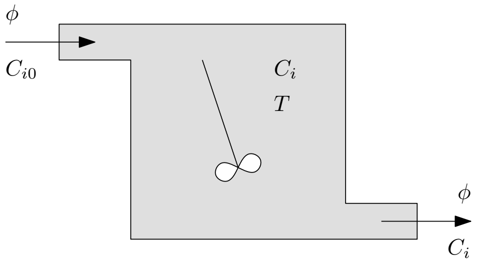

Fig. 1. Schematic of a Continuous Stirred Tank Reactor (CSTR) model.

reaction step j, measured in $\left[\text{mol } m^{-3} \; s^{-1}\right]$. The reaction rates are modeled using standard Arrhenius kinetics. For first order reactions the rates are given by (2):

$$r_j = k_j e^{-\frac{dE_j}{RT}} \prod^{\substack{\text{species}\\ \text{involved}}} C_{\text{species}} \tag{2}$$

where k_j is the pre-exponential constant, dE_j is the activation energy of the reaction step j in $\left[J \text{ mol}^{-1}\right]$, R is the gas constant in $[J \text{ mol}^{-1} \; K^{-1}]$ and T is the temperature in $[K]$.

This paper discusses catalytic reaction systems, since it will be catalyst particles that thermal energy is applied to. In a catalytic reaction system there is at least one reaction step which requires a reactant to adsorb onto a catalytic particle, before the desired reaction can proceed. An example of a catalytic reaction flow is given by (3a)-(3d). In the example, the first and second reaction steps involve an active catalytic site [1] (denoted by *). The other two reaction steps can take place without the presence of a catalytic site.

$$A + * \xrightarrow{k_1} A^* \tag{3a}$$

$$A^* \xrightarrow{k_2} B + * \tag{3b}$$

$$B \xrightarrow{k_3} C \tag{3c}$$

$$A \xrightarrow{k_4} C \tag{3d}$$

The primary reason why microwave assisted chemistry is showing improved process characteristics is commonly believed to be the uneven distribution of thermal energy in the system. The microwave irradiation causes selective heating of the catalytic particles, which are made of, or mounted on, a material which is much more susceptible for microwave irradiation than the other reactants. Therefore the heat can be modeled to be released only locally at the catalytic particles. Figure 2 shows this graphically.

The CSTR model (1) can already handle transient effects, but no spatial variation since it assumes that the reactor volume is ideally mixed. To cope with the spatial variation an extension of the model is needed.

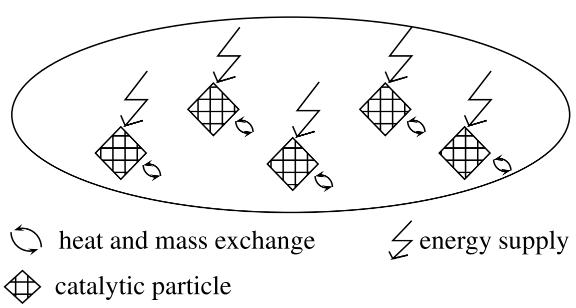

Fig. 2. Schematic representation of a reactor volume when heat is supplied directly to the catalytic particles.

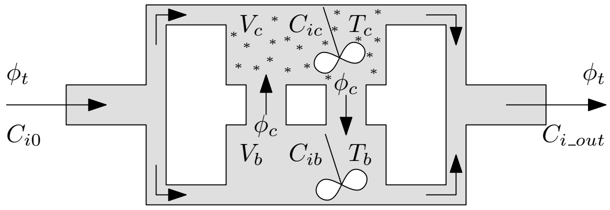

Fig. 3. Two compartment model of a catalytic reactor. The top volume (V_c) contains all the catalytic particles and their immediate surroundings, whereas the bulk volume (V_b) contains no catalytic particles.

Introducing both spatial and temporal variation creates a reaction-advection-diffusion system. Gradients of concentration/temperature create transport of mass and heat. This transport can be described by non-linear coupled partial differential equations which are derived from the conservation laws for mass and energy. The non-linear character of the equations hampers the analytical analysis of the dynamic behavior of chemical systems and make this approach less valuable for analytical research. Using numerical finite element software the partial differential equations can be discretized and solved [12].

However, there are some disadvantages to this approach. Firstly the amount of computational effort required to solve these systems can be very large. Secondly it is difficult to gain insight in the systems dynamics from the numerical results. To carry out elementary analysis of the effect of different heating regimes, a model based on a rough approximation of the partial differential equations is proposed here. Instead of modeling the reactor volume V_r as a continuous space, it is split into two sub volumes in a very specific way.

A. *The two-compartment model*

In the proposed model the catalytic particles (which are spread throughout the reactor) and their immediate surroundings which are also influenced by the heating are collected together as one volume, named the catalytic volume V_c. The remainder of the reactor volume V_r contains no catalytic particles and is assumed to be uninfluenced by the local heating of V_c, and is named the bulk volume V_b. A schematic representation of the model is shown in figure 3.

Both of the compartments are assumed to be ideally mixed, and the temperature in the catalytic volume is assumed to be a control input, while the bulk volume remains at some constant temperature. In reality there will be a temperature gradient, but in this approximation the temperature is assumed to be homogeneous throughout each volume. The input flow is spread over the bulk and catalytic volumes according to the ratio of their volumes. Since the volumes are living together in one big reactor without a physical boundary

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[1] A site is an location on the catalyst on which a reactant can adsorb.

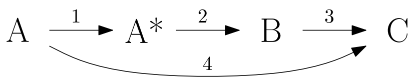

Fig. 4. Schematic of the test case reaction.

separating them, there will be transport of mass and energy between the two volumes. This transport is modeled as a flow ϕ_c. This flow includes transport by diffusion, as well as transport by convection. By assuming a large constant torrent in the reactor, ϕ_c can be approximated to be constant in time. Under these assumptions the evolutions of the volume concentrations can be modeled as two interacting CSTR models. The state evolution is given by:

$$\frac{dC_{ic}}{dt} = \frac{\phi_t}{V_r}(C_{i0} - C_{ic}) + \frac{\phi_c}{V_c}(C_{ib} - C_{ic}) + \sum_{j=1}^{N} p_{ijc} \quad \text{(4a)}$$

$$\frac{dC_{ib}}{dt} = \frac{\phi_t}{V_r}(C_{i0} - C_{ib}) + \frac{\phi_c}{V_b}(C_{ic} - C_{ib}) + \sum_{j=1}^{N} p_{ijb} \quad \text{(4b)}$$

where the subscripts 'b' and 'c' indicate 'in the bulk volume' and 'in the catalytic volume', respectively. The next step is to choose a reaction system to use in the model, such that equations can be obtained for the reaction rates of (2), which are needed to compute p_{ij}.

B. Test case reaction

The reaction that has been chosen for the simulations is a generalization of the oxidative coupling of methane (OCM), which is one of the showcase applications of microwave assisted chemistry [3]. The generalized version of the OCM reaction scheme that is used here corresponds to the reaction scheme example of (3). There are three species, which we name A,B and C. The desired product is B, which is produced from A in a catalytic reaction. Species C is a waste product. The difficulty in the OCM type reaction is that the activation energy for the adsorption of A to the catalyst is higher than the activation energy of the reactions which produce the waste product C. The reaction scheme is shown graphically in figure 4.

The rate equations for each of the reaction steps can be derived from (2). For this system the reaction rates in [mol m^{-3} s^{-1}] are given by (5). The production of individual species can easily be computed from the reaction rates.

$$r_1 = k_1 e^{\frac{-dE_1}{RT}} C_A C_* \quad \text{(5a)} \qquad r_3 = k_3 e^{\frac{-dE_3}{RT}} C_B \quad \text{(5c)}$$

$$r_2 = k_2 e^{\frac{-dE_2}{RT}} C_{A*} \quad \text{(5b)} \qquad r_4 = k_4 e^{\frac{-dE_4}{RT}} C_A \quad \text{(5d)}$$

If we assume that the activation energy dE_2 is small compared to the other activation energies, the species $A*$ will react to B almost instantaneously. In practice this means that the concentration of $A*$ will be small compared to the other species, such that it can be neglected. The reaction scheme is then reduced to the scheme as shown in figure 5. Another simplification that can be made when C_{A*} is negligible, is that the concentration of free catalytic sites C_* is constant.

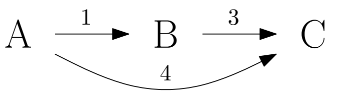

Fig. 5. Reduced schematic of the test case reaction.

TABLE I
REACTION PARAMETERS

Description	Parameter	Value	Unit
Pre-exponential factor 1	k_1	$3 \cdot 10^6$	$[m^3\text{mol}^{-1}s^{-1}]$
Activation energy 1	dE_1	$7 \cdot 10^4$	$[J\ \text{mol}^{-1}]$
Pre-exponential factor 2	k_2	large	$[s^{-1}]$
Activation energy 2	dE_2	small	$[J\ \text{mol}^{-1}]$
Pre-exponential factor 3	k_3	$3 \cdot 10^6$	$[s^{-1}]$
Activation energy 3	dE_3	$6 \cdot 10^4$	$[J\ \text{mol}^{-1}]$
Pre-exponential factor 4	k_4	$3 \cdot 10^6$	$[s^{-1}]$
Activation energy 4	dE_5	$6 \cdot 10^4$	$[J\ \text{mol}^{-1}]$

The desired reaction path is catalytic, while the undesired reaction steps are not. By reducing the volume around the catalyst particles that is heated, the undesired reactions are inhibited while the desired reaction is not. The kinetic parameters chosen for the test case reaction system are shown in Table I. These parameters are chosen in such a way that at the ambient temperature (in this case $300K$) the rates are negligible, and that the activation energy for the desired reaction is higher than that of the undesired reactions. If none of the reactions were catalytic, the undesirable rates would always dominate the desired reaction rate. But the desired reaction takes place over a catalyst, which is reflected in the model by the multiplication with the catalyst concentration for rate 1 in equation (5).

Combining the model equations of (4) with the reaction system of (5), and after including the simplifying assumptions mentioned in the previous paragraph, the total compartment model for the test case reaction is given by (6).

$$\begin{aligned}\frac{dC_{Ac}}{dt} &= \frac{\phi_t}{V_r}(C_{A0} - C_{Ac}) + \frac{\phi_c}{V_c}(C_{Ab} - C_{Ac}) \ \ldots \\ &+ (-k_1 e^{\frac{-dE_1}{RT_c}} C_{Ac} C_{*c} - k_4 e^{\frac{-dE_4}{RT_c}} C_{Ac}) \qquad \text{(6a)}\end{aligned}$$

$$\begin{aligned}\frac{dC_{Bc}}{dt} &= \frac{\phi_t}{V_r}(C_{B0} - C_{Bc}) + \frac{\phi_c}{V_c}(C_{Bb} - C_{Bc}) \ \ldots \\ &+ (k_1 e^{\frac{-dE_1}{RT_c}} C_{Ac} C_{*c} - k_3 e^{\frac{-dE_3}{RT_c}} C_{Bc}) \qquad \text{(6b)}\end{aligned}$$

$$\begin{aligned}\frac{dC_{Cc}}{dt} &= \frac{\phi_t}{V_r}(C_{C0} - C_{Cc}) + \frac{\phi_c}{V_c}(C_{Cb} - C_{Cc}) \ \ldots \\ &+ (k_3 e^{\frac{-dE_3}{RT_c}} C_{Bc} + k_4 e^{\frac{-dE_4}{RT_c}} C_{Ac}) \qquad \text{(6c)}\end{aligned}$$

$$\begin{aligned}\frac{dC_{Ab}}{dt} &= \frac{\phi_t}{V_r}(C_{A0} - C_{Ab}) + \frac{\phi_c}{V_b}(C_{Ac} - C_{Ab}) \ \ldots \\ &+ (-k_4 e^{\frac{-dE_4}{RT_b}} C_{Ab}) \qquad \text{(6d)}\end{aligned}$$

$$\begin{aligned}\frac{dC_{Bb}}{dt} &= \frac{\phi_t}{V_r}(C_{B0} - C_{Bb}) + \frac{\phi_c}{V_b}(C_{Bc} - C_{Bb}) \ \ldots \\ &+ (-k_3 e^{\frac{-dE_3}{RT_b}} C_{Bb}) \qquad \text{(6e)}\end{aligned}$$

$$\begin{aligned}\frac{dC_{Cb}}{dt} &= \frac{\phi_t}{V_r}(C_{C0} - C_{Cb}) + \frac{\phi_c}{V_b}(C_{Cc} - C_{Cb}) \ \ldots \\ &+ (k_3 e^{\frac{-dE_3}{RT_b}} C_{Bc} + k_4 e^{\frac{-dE_4}{RT_b}} C_{Ab}) \qquad \text{(6f)}\end{aligned}$$

TABLE II

SIMULATION PARAMETERS

Description	Parameter	Value	Unit
Reactor Volume	V_r	1	$\left[m^3\right]$
Gas Constant	R	8.314	$\left[J\text{mol}^{-1}K^{-1}\right]$
Amount of Sites	N	1	[mol]
Ambient/Bulk Temperature	T_b	300	$[K]$
Inter Volume Flow	ϕ_c	0.2	$\left[m^3\ s^{-1}\right]$
Input Concentration A	C_{A0}	1	$\left[\text{mol}\ m^{-3}\right]$
Input Concentrations B,C	C_{B0}, C_{C0}	0	$\left[\text{mol}\ m^{-3}\right]$

In this section the compartment model has been developed, and the test case reaction has been introduced. The next sections describe simulations with the test case reaction in the compartment model. First, effects of local heating are shown in section III, and subsequently effects of transient (pulsed) local heating are shown in section IV.

III. LOCAL CONTROL OF CATALYTIC REACTION SYSTEM

In this section results are presented of simulations of the two compartment model equations of (6) under steady state conditions. The simulations show the expected results when the heated volume is less than the complete volume V_r. The parameters used for the constants used in the simulation are listed in table II. The inter volume flow ϕ_c is assumed to be constant as well.

A. Steady state analysis

In this subsection the steady states of (6) are analyzed for constant values of the inputs ϕ_t and T_c. Closer inspection of the model equations shows that when the inputs are fixed, (6) reduces to a set of linear equations in the reactant concentrations. This set of equations will have a unique solution which can easily be computed. When solving (6) for constant inputs, the results are given by (10) on page 5. In (10), the reaction rates have been substituted by a shorthand versions for shorter notation. The shorthand versions are defined in (7).

$$q_1 = k_1 e^{\frac{-dE_1}{RT_c}} C_{*c} \tag{7a}$$

$$q_2 = k_3 e^{\frac{-dE_3}{RT_c}} \tag{7b}$$

$$q_3 = k_4 e^{\frac{-dE_4}{RT_c}} \tag{7c}$$

$$q_4 = 0 \tag{7d}$$

$$q_5 = k_3 e^{\frac{-dE_3}{RT_b}} \tag{7e}$$

$$q_6 = k_4 e^{\frac{-dE_4}{RT_b}} \tag{7f}$$

B. Optimal steady state

Chemical engineerings typically measure the performance of a reactor by several indicative values. The total yield of desired product is an important measure, as is the selectivity of the reaction toward the desired reaction. The yield Y is defined as the total amount of product B flowing out of the reactor each second. The selectivity S is defined as the ratio of desired product over total amount of reacted input material. In terms of the two compartment model in steady state, the yield and selectivity are given by (8) and (9):

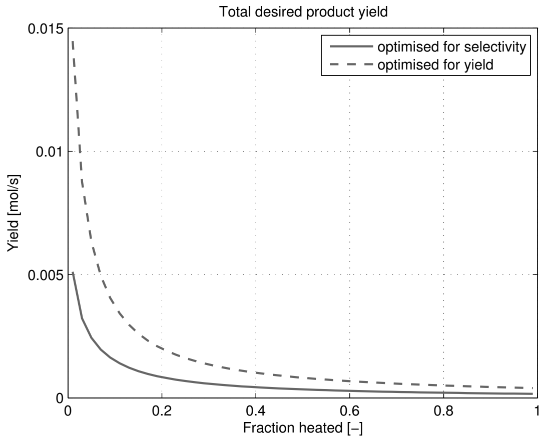

Fig. 6. Total product yield plotted against the size of the heated volume for different input strategies.

$$Y = \frac{\phi_t (V_b C_{bb\_ss} + V_c C_{bc\_ss})}{V_r} \tag{8}$$

$$S = \frac{V_b C_{bb\_ss} + V_c C_{bc\_ss}}{V_r C_{A0} - V_b C_{ab\_ss} - V_c C_{ac\_ss}} \tag{9}$$

The inputs ϕ_t and T_c are not fixed can be used to optimize the yield and selectivity criteria. An analytical optimization analysis is not straightforward through the strong nonlinearities in (10). Therefore the inputs have been optimized through numerical optimization. The optimization was subjected to a constraint $V_r/3600 \leq \phi_t \leq V_r/30$ (residence time somewhere between 30 seconds and one hour). Though we cannot prove it, it looks like the optimum for both selectivity and yield always lies at the maximum allowed value for ϕ_t. The optimal temperatures are different for both cases though.

Figure 6 shows the yield of product B for various sizes of heated catalytic volume V_c. The inputs have been chosen such that they optimize the yield, or the selectivity. Figure 7 shows the selectivity toward the product B, also plotted against the size of the heated catalytic volume, and also for optimized inputs ϕ_t and T_c.

These plots clearly show that the optimal results are better when the heated volume is small. When V_c is close to V_r, hardly any yield is possible because so much C is produced. When the heated volume V_c around the catalyst particles is small, both the optimal yield and the optimal selectivity increase significantly. The reason for this is that the V_c by definition contains all catalyst particles, and when V_c becomes smaller the concentration of catalyst particles C_{*c} becomes larger. These two effects cancel such that the net production of B in $\left[\text{mol } s^{-1}\right]$ remains the same. Since the undesired reactions take place in any heated volume, the total production of undesired product for smaller V_c does decrease when V_c decreases.

IV. PERIODIC CONTROL OF CATALYTIC VOLUME

Periodic control of input variables such as feed concentration or reactor temperature is a form of process intensification

$$C_{Ab\_ss} = \frac{\phi_t V_b(\phi_t V_c + \phi_c V_r + V_c V_r(q_1 + q_3)) + \phi_c \phi_t V_c V_r}{(\phi_t V_b + V_b V_r q_6)(\phi_t V_c + \phi_c V_r + V_c V_r(q_1 + q_3)) + \phi_c V_r(\phi_t V_c + V_c V_r(q_1 + q_3))} C_{A0} \tag{10a}$$

$$C_{Ac\_ss} = \frac{\phi_t V_c}{\phi_t V_c + \phi_c V_r + V_c V_r(q_1 + q_3)} C_{A0} + \frac{\phi_c V_r}{\phi_t V_c + \phi_c V_r + V_c V_r(q_1 + q_3)} C_{Ab\_ss} \tag{10b}$$

$$C_{Bb\_ss} = \frac{\phi_c V_c V_r^2 q_1}{(\phi_t V_b + V_b V_r q_5)(\phi_t V_c + \phi_c V_c + \phi_c V_r + V_c V_r q_2) + \phi_c V_r(\phi_t V_c + V_c V_r q_2)} C_{Ac\_ss} \tag{10c}$$

$$C_{Bc\_ss} = \frac{\phi_c V_r}{\phi_t V_c + \phi_c V_r + V_c V_r q_2} C_{Bb\_ss} + \frac{V_c V_r q_1}{\phi_t V_c + \phi_c V_r + V_c V_r q_2} C_{Ac\_ss} \tag{10d}$$

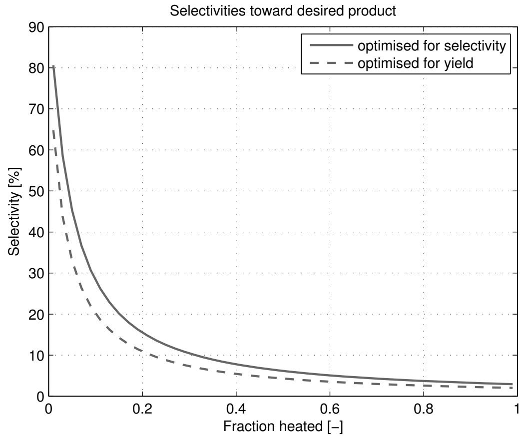

Fig. 7. Selectivity toward the desired product plotted against the size of the heated volume for different input strategies.

which can improve reaction characteristics. Because the time constants for heating/cooling in large reactors are typically large, feed concentration variation is more commonly applied. In case only the catalyst volume is heated as in the previous sections, the amount of energy needed to quickly heat this volume is small and periodic temperature control becomes an interesting option.

In [13] there is a theoretical exploration of the optimal inputs for reactions of A, B and C in continuous stirred tank reactors (CSTR). The result of that analysis is that the optimal temperature input profile is of bang-bang type when the activation energy of the desired reaction is higher than that of parallel or consecutive reactions. When the catalytic volume in our model is small compared to the bulk volume, the catalytic volume can be approximated by a CSTR model.

This section shows results of simulating the two compartment model when the catalytic volume V_c is small compared to the total reactor volume V_r, with the catalytic volume subjected to a bang-bang type temperature profile. More specifically, in this section we take $V_c = 0.01m^3$, with all the other reaction and reactor parameters identical to those in section III.

A. Periodic input definitions

The input is pulsed with period time τ in $[s]$. During the first part of each period (up to time t_{pulse}) the temperature is high, and the rest of the period the temperature is low (equal to the ambient temperature). This behavior is described by (11):

$$T_c(t) = \begin{cases} T_{high}, & \text{for } t \leq t_{pulse} \mod \tau \quad (11a) \\ T_{amb}, & \text{for } t > t_{pulse} \mod \tau \quad (11b) \end{cases}$$

Since the temperature input profile for the catalytic volume is now pulsed repeatedly, the states of the model will not converge to a steady state. However, the system switches between two stable linear systems, it can be shown all of the states themselves will become periodic as well. The instantaneous yield and selectivity can be evaluated at any time, but since these quantities will also become periodic, it is useful to redefine them to be averaged over a whole period.

$$Y^p = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} \frac{\phi_t(V_b C_{bb}(t) + V_c C_{bc}(t))}{V_r}\, dt \tag{12}$$

$$S^p = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} \frac{V_b C_{bb}(t) + V_c C_{bc}(t)}{V_r C_{A0} - V_b C_{ab}(t) - V_c C_{ac}(t)} dt \tag{13}$$

$$T^p = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} T_c(t)\, dt \tag{14}$$

where the superscript 'p' indicates the periodic case.

B. Periodic input optimization

Finding the optimal periodic input is a harder problem than finding the optimal input for the steady state case. It is suggested in [13] that the optimal input profile consists of infinitely short pulses. Therefore the pulse length t_{pulse} is set to a small, but still feasible value. More specifically, $t_{pulse} = 10\ ms$. For this pulse length Y^p and S^p can be numerically optimized with respect to the pulse temperature T_{high} and pulse period τ.

Numerical optimization gives the parameters in table III as optimal inputs for yield an selectivity. The optimal selectivity is 85%, at a yield of $2.8 \cdot 10^{-3}$mols^{-1}. The optimal yield is $15.4 \cdot 10^{-3}$mols^{-1}, at a selectivity of 68%. The resulting plots of the catalyst volume concentrations are plotted in figures 8 and 9. The bulk volumes hardly vary during a pulse, so they are not plotted.

These results make both the optimum yield and the optimum selectivity slightly higher than the optimum obtainable from selective heating alone, as can be seen by comparing to the results in section III. However the largest difference is in the average temperature, which is a lot lower in the periodic

TABLE III

OPTIMAL PERIODIC INPUT PARAMETERS

Description	Parameter	Value	Unit
Yield optimizing			
Pulse period	τ	0.079	$[s]$
Pulse temperature	T_{high}	560	$[K]$
Selectivity optimizing			
Pulse period	τ	1.50	$[s]$
Pulse temperature	T_{high}	550	$[K]$

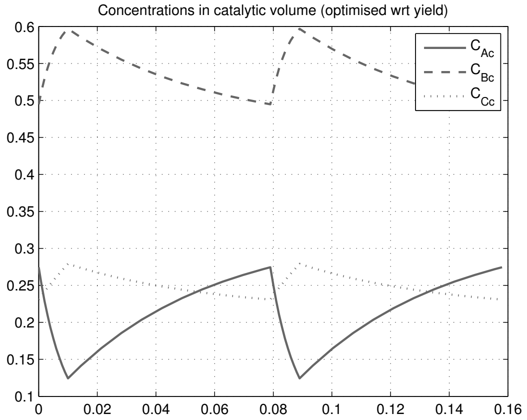

Fig. 8. Concentrations in catalytic volume in time, when inputs are optimized for yield.

control case. The pulse temperature T_{high} is higher than the temperatures for selective steady state heating, but the pulse width is only very short, such that the average temperature is lower. This means that the total amount of energy required to operate the reactor in pulsed mode will be smaller than for steady state operation.

V. CONCLUSION AND OUTLOOK

A two-compartment model has been developed to investigate the effects of local and transient control of catalytic reaction systems. One of the two compartments contains all the catalytic particles, and hence the catalytic reactions can only take place in this volume. The test case reaction chosen is a generalized version of the oxidative coupling of methane (OCM), which is notoriously 'difficult'. In this system there are non-catalytic reactions which result in the production of a waste product, which are activated more easily than the reaction which produces the desired product.

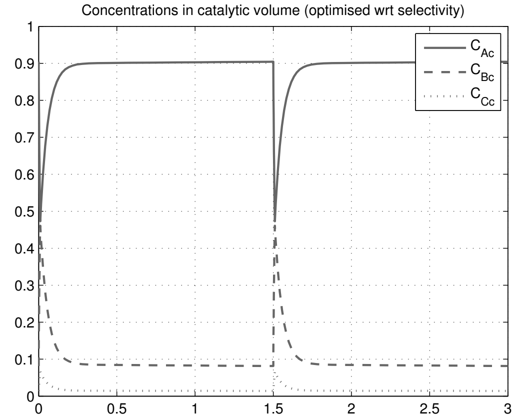

Fig. 9. Concentrations in catalytic volume in time, when inputs are optimized for selectivity.

It has been shown through simulations in section III that when the size of the heated catalytic volume is varied while keeping the amount of catalyst particles equal, the model predicts an increase in obtainable selectivity as well as an increase in obtainable product yield. The main reason is that the desired reaction is not hampered by the local heating, while the undesired reactions are. These results were expected since the OCM reaction is one of the showcase applications of microwave assisted chemistry.

In section IV the local steady state heating was extended to periodic local heating. Through optimization of the input temperature in a given local volume it is shown that the reaction characteristics can be improved upon even further by applying periodic heating to the local volume.

The local and periodic energy supply gives best results for reactions which suffer from competing reactions which are activated more easily than the desired reactions. Because the yield and selectivity using traditional global steady state heating approach are poor, it may not be profitable to operate these reactions using this traditional approach. This approach is a promising concept, which may very well allow these reaction systems to be operated profitably in the future.

A prototype reactor is currently under development to validate the simulation results obtained with the model.

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