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Perspectives on control of heterogeneous catalytic chemical reactions by manipulation of non-uniform temperature

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***Abstract*—The application of non-uniform process conditions in chemical heterogeneous[1] catalytic reactions is suggested as innovative way to enhance the controlability of this class of chemical reactions. By use of first principle models, the perspectives of this idea are researched. It is shown that the application of non-uniform and unsteady process conditions can lead to a valuable new technique to apply control to chemical reactions and to influence process or product properties.**

***Index Terms*—Pulsed heating, unsteady operation, non-uniform conditions, transient conditions, heterogeneous catalysis, selectivity control, selective heating.**

I. INTRODUCTION

Chemistry has an enormous impact on modern social life. Chemistry is involved in the production of almost any product and enormous amounts of raw materials and energy are consumed in this branch of industry. As a result of the continuously increasing consciousness to save the environment and the decreasing availability of raw materials, the wish to create environmentally sound processes increases and optimization of plants and production methods becomes an issue, more and more.

The development of good models for chemical processes which are valid in a wide operation range and suitable for optimisation is very complicated. Chemical interaction between matter can be studied on a wide range of dimensional scales and time scales. The interaction between individual molecules is studied at nanometer scale, while in chemical industry chemical reactions are carried out in plants with sizes in a range of fractions of centimeters to hundreds of meters. Chemical reactions are inextricably connected with the change of thermodynamic states and fluid dynamics, which introduces non-linearity and dependency on geometric dimensions. Furthermore, due to the complicated (non-linear) interaction between the variables in these fields and difficulties of measuring them accurately, it is difficult to verify the models and identify their parameters.

Obviously, the lack of accurate models has a large impact on the development of chemical plants and the way they are operated nowadays. Many processes show unstable behavior under certain process conditions and the enormous dimensions of plants in industry make it difficult to apply control to these processes. Therefore, many chemical processes are operated under steady state and mild conditions such that reliable and safe operation can be guaranteed. On the other hand, there is a large demand on flexibility in the operation of plants. Normally, the startup of processes takes days and it takes many hours to change the desired operation conditions. Considering the large expenses of building chemical plants, the flexibility with respect to wear, weather, feedstock composition and product specifications forms an important design constraint. Furthermore, theoretically [2]–[4] and experimentally [5], [6] it has been shown that operation under time varying process conditions may have big advantages. For example, under time varying process conditions reaction rates and selectivity with respect to the desired product can be increased.

It can be concluded that one would wish accurate and fast control over the chemical reactions taking place. In literature it is remarked several times that the nonlinear relationship between reaction rate and temperature suggests that temperature is a suitable parameter to apply control to [9].

In general, it is assumed that the relationship between temperature (T) and reaction rate (R_i) for elementary reaction steps is properly described by the Arrhenius equation [1], [7]:

$$R_i = k_i e^{\frac{-E_i}{R_g T}} \tag{1}$$

From the non-linear character of the Arrhenius equation it follows that a small change in temperature can result in a large change of the reaction rate. On the other hand, large chemical systems are often dominated by slow thermal dynamics which make the realisation of dynamic operation difficult. An attempt to overcome the large time constants of classical plants is made by the recent development of micro reactors [9]–[12].

The validity of the Arrhenius equation can be made plausible by statistical analysis of collision models used in dynamic gas theory. Chemical interactions between molecules are in essence the result of collisions between the molecules, which happen on a very small time and geometry scale. In order to result in chemical interaction between the molecules, the translational energy of the colliding molecules has to be larger than a certain energy barrier [7]. For the derivation of the Arrhenius equation, it is assumed that molecules in a system are at thermodynamic equilibrium and have a translational energy distribution according to the Boltzmann distribution [1], [8].

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[1] The term heterogeneous refers to the difference in thermodynamic phase between the catalyst and the reaction mixture [1].

The Boltzmann distribution is the velocity distribution for a system with N molecules that has the largest entropy (S) and can be derived from the Boltzmann principle:

$$S = k_B \log W(E, N), \qquad (2)$$

where:
W = The number of microscopic ways a system with energy E and N molecules can be ordered,
k_B = Boltzmann's constant.

In figure 1, the velocity probability distribution for helium molecules at four temperatures is shown. At moderate temperatures only a small fraction of molecules has such a high translational energy, that they have the potential to participate in collisions that result in reactions. If the system is observed at one time instant, the rest of the molecules carries energy but will not participate in the reaction. On the other hand, these molecules contain energy and contribute to the thermal time constant of a system.

This observation has lead to the idea that it would be ideal if one would be able to supply energy to only a part of the molecules in such way that all the molecules that are accelerated by this energy, have a large probability to react. When the supply of energy stops and time passes, the energy will be distributed over the total reactant and the probability on effective collisions will decay.

Most of the reactions are carried out by use of catalysts. Heterogeneous catalysts introduce spatial non-uniformity to a system. In heterogeneous catalytic reactions, the location where reactions take place is perfectly defined; by definition, essential steps of the desired reaction take place at the catalytic surface. In the bulk material, consecutive and competitive reactions take place. If the bulk temperature could be low such that reactions do not proceed here, while environment of the catalyst site is at a temperature such that reactions here do proceed, large improvements in selectivity might be made. When unsteady and selective heating is applied to heterogeneous catalysts, this might have even larger advantages for the control of reactions.

Only a few publications on the application of pulsed heating of catalysts has been found in literature. In a series of papers [13]–[20] and patents [21]–[24] by Wan et al., experiments are described where chemical catalytic reactions and pulsed supply of high power microwave radiation are combined with the aim to initiate reactions at the catalysts sites while the bulk remains cold. The papers report about experiments where excellent selectivity and reaction rates are achieved but do not study unsteady non-uniform heating with the aim to apply control to the reaction. The research by Wan et al. is mostly experimental work where explanation of the observed effects is based on the observations. A clear theoretical model is not given.

Investigation of the perspectives on non-uniform and time variant heating with the aim to control chemical catalytic reactions is one of the projects that is currently carried out in the Tu/e Control Systems group. In this paper we present the first results of this research. In the next section the problem statement will be described more formally. In the subsequent sections different aspects of unsteady and non-uniform heating will be investigated by use of dynamic models.

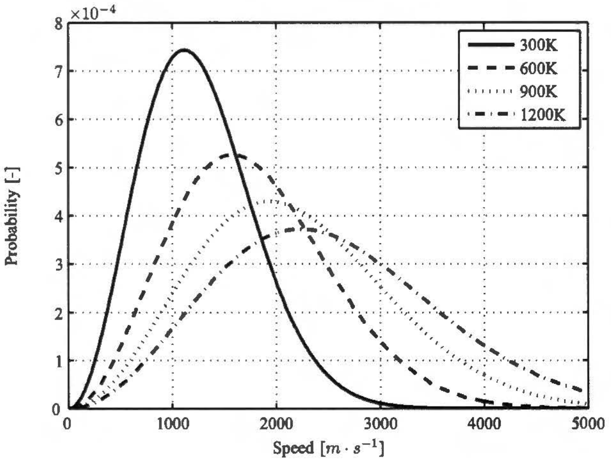

Fig. 1: Relation between molecule velocities and their probabilities according to the Boltzmann distribution for helium molecules at four temperatures.

II. PROBLEM STATEMENT

Based on the given reasoning, the pulsed heating of a reactant is expected to have advantages for the controlability of the reactions. The effects which are expected to show up are formulated as the hypotheses. The research will be based on these hypotheses on. The hypotheses are:

1) Localised supply of energy to a part of reactant enables to create local conditions that differ from the bulk conditions. Selective supply of energy to heat a catalysts surface accelerates reactions at the catalyst surface, while the bulk temperature can be kept low and side reactions do not show up. As a result of this:
    a) The reaction can be carried out at more friendly process conditions. The average temperature of the total system or the operating pressure can be lower to achieve the same conversion rate.
    b) Selectivity of reactions can be influenced to a level that is not achievable under homogeneous energy supply.
2) By the unsteady supply of energy to a catalyst to heat a catalyst surface one can interact with the dynamics of transport processes at the catalysts surface and in the catalysts neighbourhood. As a result of this:
    a) The course, the selectivity or the conversion rate of the reaction can be influenced in a way that is not possible under steady energy supply.
    b) Energy is used more efficiently with respect to continuous energy supply.

This paper presents the first research done in order to investigate validity of hypotheses 1 and 2. With use of a basic model the effect of non-uniform pulsed heating on a chemical reacting system is studied. Subsequent the effect of temperature variation on a chemical reacting system is investigated. Finally, the effect of dimensional scaling on the dynamic behavior of non-uniform energy distribution in a reacting system is investigated. The emphasis of the models is on the dynamic behavior on the system. Although the used chemical parameters and mechanisms are chosen carefully, their exactness will not be discussed.

III. NON-UNIFORM REACTIONS

Under non-homogenous circumstances gradients in concentration and temperature show up. These gradients are the driving force for diffusive transport of mass and energy. The reason to study perspectives on non-uniform temperatures in reacting systems is based on the idea that the dynamic change of local concentrations and temperature caused by these transport phenomena can be used to our advantage. The dynamic behavior of non-uniform quantities can be modelled by use as a reaction diffusion convection model based on partial differential equations. For a chemical reacting system the equations have the general form [25]:

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T + \vec{a} \nabla T + \frac{1}{\rho c_p} \sum_{i=1}^{j} -\Delta H_i r_i \tag{3a}$$

$$\frac{\partial C}{\partial t} = D_C \nabla^2 C + \vec{a} \nabla C + r_i \tag{3b}$$

$$r_i = f_i R_i \tag{3c}$$

Heterogeneous catalytic reactions by definition take place at the catalysts sites, which introduces spatial dependence to the system. Spatial dependence in the reacting system can be incorporated in the model (3) by making the parameters D_T, D_C and reaction term r_i dependant on space.

Although a nice mathematical description of a system can be given by equations like (3), the non-linearity in the reaction term of the equations hampers the analytical analysis of these systems. Due to the non-linear and stiff character of the problem, simulations based on spatial discretisation of the partial differential equation are not trivial and in general time consuming. Moreover, the non-negativity constraint on the states complicates the numerical integration of the equations as it can result in instabilities of numerical schemes [26].

In order to show the effect of local heating and an unsteady temperature of the vicinity of the catalyst on the chemical reaction, a model based on first principles has been made. In this model, the direct vicinity of a heated catalyst and its environment i.e. the bulk are modelled as separate volumes. The catalyst is considered as a element with dynamics which preforms some chemical transformation in a small region around it. Such a reacting zone around the catalyst, which is interacting with its environment (e.g. the bulk) is shown in figure 2.

A. First principle model

The abstract view on a catalyst shown in figure 2, serves as basis for a first principle model that has been developed. The vicinity of the catalyst and the bulk are modelled as two ideally mixed interacting volumes, shown in figure 3. It is assumed that there is a large mixing force in the bulk, which enforces a flow that exchanges mass and heat between the catalyst and bulk. The exchange of heat and mass between the volumes is modelled as a flow ϕ_c. The bulk is coupled to an environment with fixed quantities by a fixed flow ϕ_f. Heat can be applied to the volume with the catalyst by a power source q_{in}. In section IV the influence of temperature changes on the course of the reaction in the catalytic volume will be investigated. In the next part of this section the effect of selective pulsed heating on a catalytic reaction will be investigated.

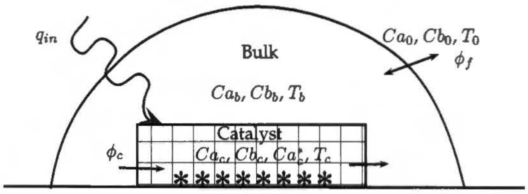

Fig. 2: Visualisation of interaction between reacting zone of catalyst and its environment. In general, the geometry of the catalyst is not restricted to a slab and the catalyst does not have to be supported.

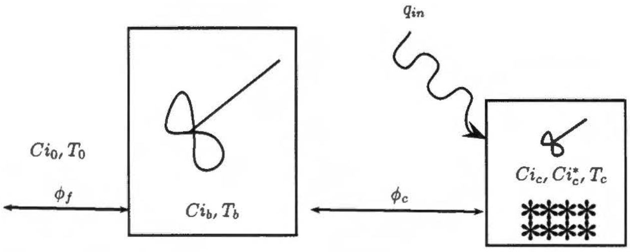

Fig. 3: First principle model used for analysis.

B. Testcase

A test case has been set up with use of the model, to investigate the difference behavior of a reaction under pulsed heating of the catalyst, steady heating of the catalyst and uniform heating of the bulk and catalyst. In the system two competing reactions according to the mechanism (4) are carried out. The reaction product D produced by the catalytic reaction is desired while the product C of the competing reaction in the bulk has to be minimised. The catalytic reaction steps follow the Langmuir-Hinshelwood kinetics [27]. It is assumed that the desorption step of product D is infinitely fast. The activation energy of step (4d) is higher that the activation energy of the other steps and the frequency factors of the desired steps are ten times lower than the frequency factor of the competitive reaction.

$$A \xrightarrow{k_1^+} C \tag{4a}$$

$$A + * \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} A^* \tag{4b}$$

$$B + * \underset{k_3^-}{\overset{k_3^+}{\rightleftharpoons}} B^* \tag{4c}$$

$$A^* + B^* \xrightarrow{k_4^+} D + 2* \tag{4d}$$

All sites which are physically present in the volume V_R are modelled as being positioned in the catalytic volume. For the volume V_R a concentration of $N_R[\mathrm{mol} \cdot \mathrm{m}^{-3}]$ is chosen. Therefor, the site concentration in the catalytic volume V_C equals $N_C = N_R \frac{V_R}{V_C}$, such that the total number of sites is preserved. The catalytic volume is a hundred times smaller than the reactor volume. In table I all parameters are shown.

The dynamic model of the system is given in appendix C. The model has been implemented as a level-2 s-function in Matlab Simulink, and solved with the ode15s solver with a relative error tolerance of 10^{-5}. Again, the non-negativity constraint on the states makes time integration difficult. During the simulation the states are checked to remain positive to ensure reliability of the solution.

Three simulations with different heating strategies have been carried out with the model. In the first simulation the total reactor is kept at a constant temperature, in the second case a constant amount of heat is supplied to the catalytic volume and in the third case the heat is supplied to the catalytic volume in a pulsed manner. The pulses are applied with a frequency of 1 Hz and a duty cycle of 2.5%. The amplitude varies between 100W and 5200W. The time average value of the states in the bulk are calculated to compare the different ways of operation. An initial value of zero for all states is used to start the simulations. The time average of the concentrations and temperature has been calculated from the point from periodic which behavior was observed. In figures 5a and 5b the relation between the average temperature and average bulk temperature is shown. The selectivity $\bar{S}$, shown in figure 5c, has been defined as the ratio of average concentrations of products:

$$\bar{S} = \frac{\bar{C}_c}{\bar{C}_c + \bar{C}_d}. \tag{5}$$

From figures 5b and 5c it follows that the concentration of D and the reaction selectivity can be influenced by operation under unsteady temperature. From figure 5c it follows that selective heating of the catalyst enables to preform the reaction with much higher selectivity, which is in agreement with the hypotheses. By use of pulsed selective heating, a transient high temperature can be realised in the catalytic volume. Due to the non-linear relation between temperature and reaction rate, this results in a high average reaction rate in the catalytic volume while the bulk stays cold and the reaction there does not proceed. Although the used model is a quite rough approximation of the reality, it shows the potential of selective and pulsed heating. The model can easily be extended to a more precise model. With of more volumes, gradients and transport mechanisms such as diffusion can be modelled in more detail. Furthermore, the model can be extended to other reactions mechanism, like polymerisation and competing reactions at the catalyst sites.

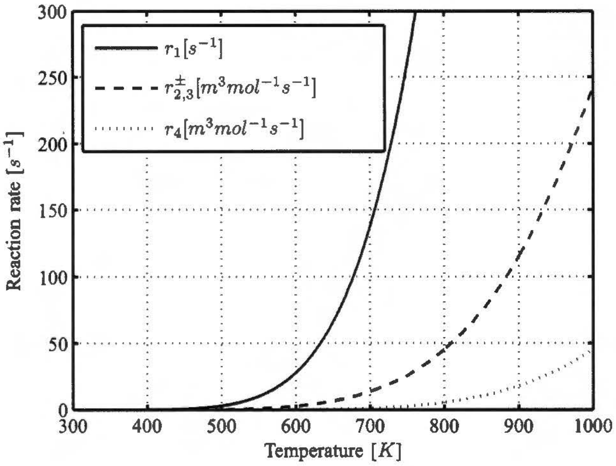

Fig. 4: Relation between temperature and reaction rates of the reaction steps.

IV. CONSECUTIVE REACTION UNDER PULSED TEMPERATURE CONTROL

Hypothesis 2 is based on the idea that dynamics of a system can be used to influence the course of chemical reactions. The effect of periodically changing temperature of a continuous stirred tank reactor[2] with consecutive reactions is investigated as preparation for the investigation of two interacting CSTR-models with catalytic reactions in one of them.

Consecutive reactions take place in many processes and are typically modelled by mechanism (6). In many industrial applications, the intermediate product B is the desired product while the final product C is less valuable or is waste. Optimization with respect to product B is most challenging if the activation energy of step 1 in the reaction is larger than the activation energy of step 2, which is assumed in this section.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{6}$$

The dynamics of a CSTR in which reaction (6) is carried out, are described by the dimensionless equations (7). Derivation of these equations is given in appendix B.

$$\frac{d\chi_A}{d\tau} = - y\chi_A + u_n(1 - \chi_A), \tag{7a}$$

$$\frac{d\chi_B}{d\tau} = y\chi_A - ky^E\chi_B - u_n\chi_B, \tag{7b}$$

$$\frac{d\chi_C}{d\tau} = ky^E\chi_B - u_n\chi_C, \tag{7c}$$

It is assumed that the temperature is an ideally controllable quantity, such that it becomes a parameter of the system. In the series of papers by Matsubara [4], [28], [29], it has been

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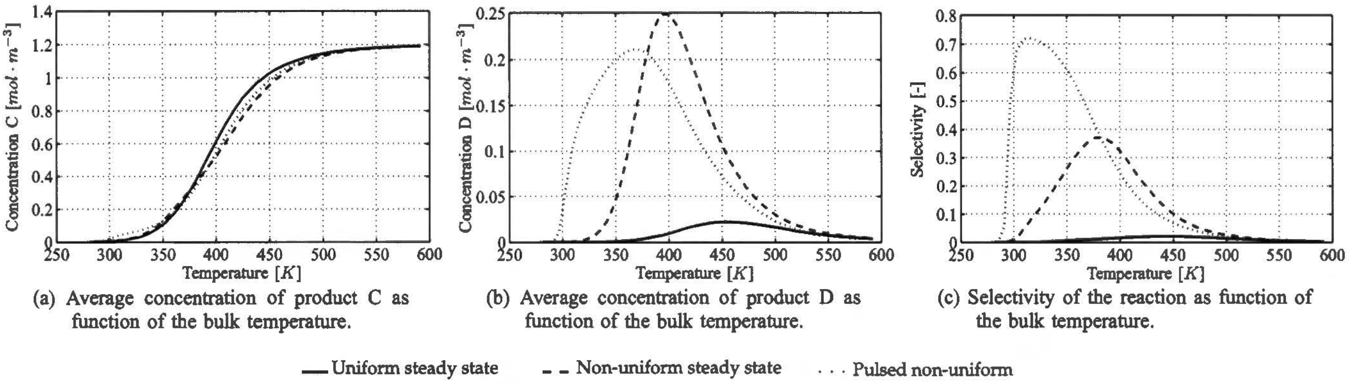
[2] abbreviated to CSTR, see [1] for an introduction.



(a) Average concentration of product C as function of the bulk temperature.

(b) Average concentration of product D as function of the bulk temperature.

(c) Selectivity of the reaction as function of the bulk temperature.

Fig. 5: Relation between temperature and reaction rates of the reaction steps.

shown with use of optimal control theory that for a consecutive reaction with $E < 1$an increase in average concentration can be achieved by temperature variation. The optimal temperature profile is then achieved by fast switching between the highest and lowest allowed temperature. This type of control is sometimes called bang-bang control. The operation under constant temperature is investigated in this section and subsequently compared with operation under periodic temperature change. When the temperature of the CSTR is switched between T_{pulse} and T_{low}, the parameters in the system dynamics change according Arrhenius equations which describe these parameters. The behaviour under temperature switching will be analysed as if there are two dynamical systems between which is switched when the temperature changes. The state at the end of a time interval is the initial condition for the dynamic system describing the subsequent time interval. Both dynamic systems will be investigated and the conclusions will be combined in the section on periodic temperature switching. An algorithm for calculation of the maximal achievable yield under temperature switching is given. In order to compare steady and unsteady operation fairly, all system parameters except the temperature are kept constant in the analysis.

Two measures have been defined to compare the operation of the CSTR under different conditions. The instantaneous yield $(Y_i(\tau))$ represents the amount of species i flowing out of the reactor at time τ:

$$Y_i(\tau) = u_n(\tau)\chi_i(\tau) \tag{8}$$

In order to compare the steady and unsteady analysis the average yield has been defined by the equation (9).

$$\bar{Y}_i(\tau) = \frac{1}{\tau}\int_0^{\tau} Y_i(\zeta)d\zeta \tag{9}$$

The selectivity $(\bar{S}_i(\tau))$ of the reaction with respect to species i, can be defined in several ways [30]. Here, the selectivity of the reaction is defined as the ratio between the amount obtained desired product and the amount of total of obtain converted reactant. For the reaction under study, the selectivity with respect to product i is defined as:

$$\bar{S}_i(\tau) = \frac{\bar{Y}_i(\tau)}{\sum\limits_{j \in \text{products}} \bar{Y}_j(\tau)}. \tag{10}$$

In this section the flow is assumed to be constant in time. Under this condition, the selectivity with respect to product B under steady state operation can be rewritten to:

$$\bar{S}_B = \frac{\chi_B}{\chi_B + \chi_C}. \tag{11}$$

The conditions for optimality of selectivity and yield can be contradicting. Therefore, the best operation conditions can only be determined if the context of the process is known.

A. Steady state analysis

The steady state operation of the system is used as reference for the performance under periodic operation. The concentrations in steady state (χ_{ss}) are described by the equations:

$$\chi_{Ass} = \frac{u_n}{y + u_n}, \tag{12a}$$

$$\chi_{Bss} = \frac{y u_n}{(y + u_n)(k y^E + u_n)}, \tag{12b}$$

$$\chi_{Css} = \frac{k y^{E+1}}{(y + u_n)(k y^E + u_n)}. \tag{12c}$$

In the steady state, the selectivity with respect to product B and yield is given by:

$$S_{Bss} = \frac{u_n}{u_n + k y^E}, \tag{13}$$

$$Y_{Bss} = \frac{y u_n^2}{(y + u_n)(k y^E + u_n)}. \tag{14}$$

The concentrations in steady state depend on both the temperature and the flow. Figure 6 shows that for each temperature there is a value for the flow such that concentration χ_B is maximised. Maximisation of χ_{Bss} as function of u_n shows that the maximum concentration is achieved if:

$$\hat{u}_n = \sqrt{k y^{E+1}}. \tag{15}$$

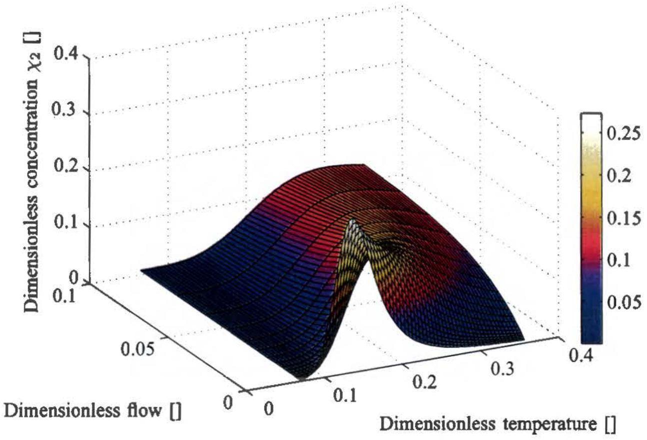


Fig. 6: Steady state concentration χ_{Bss} as function of temperature and flow for a system with parameter shown in table II. For each temperature a unique maximum exists.

If the system is operated with the optimal flow for a given temperature, the concentrations are given by:

$$\hat{\chi}_{Ass} = \frac{\sqrt{ky^{E-1}}}{1+\sqrt{ky^{E-1}}} \tag{16a}$$

$$\hat{\chi}_{Bss} = \frac{1}{(1+\sqrt{ky^{E-1}})^2} \tag{16b}$$

$$\hat{\chi}_{Css} = \frac{ky^{E}\sqrt{ky^{E-1}}}{(1+\sqrt{ky^{E-1}})^2} \tag{16c}$$

Under these operation parameters the yield of product B and selectivity with respect to B can be calculated by combination of equation (15) with (13) resp. (14), resulting in:

$$S_{Bss}|_{u_n=\hat{u}_n} = \sqrt{\hat{\chi}_{Bss}} \tag{17}$$

and

$$Y_{Bss}|_{u_n=\hat{u}_n} = \frac{\sqrt{ky^{E+1}}}{(1+\sqrt{ky^{E-1}})^2} \tag{18}$$

B. Influence of temperature

It is assumed that the influence of the variation between the temperature is large such that at the lowest temperature the system dynamics are dominated by the flow and that at highest the temperature the system dynamics are dictated by the chemical terms. Under this assumption, the dynamics for the system at high temperature can be described by neglecting the flow terms from the equations of the overall dynamic system, and the approximated system can be described by:

$$\frac{d\chi_A}{d\tau} = -\,y\chi_A, \tag{19a}$$

$$\frac{d\chi_B}{d\tau} = y\chi_A - ky^E\chi_B, \tag{19b}$$

$$\frac{d\chi_C}{d\tau} = ky^E\chi_B. \tag{19c}$$

In contrast, the system at the low temperature can be described by neglecting of the chemical reaction terms, resulting in the equations:

$$\frac{d\chi_A}{d\tau} = u_n(1-\chi_A), \tag{20a}$$

$$\frac{d\chi_B}{d\tau} = -\,u_n\chi_B, \tag{20b}$$

$$\frac{d\chi_C}{d\tau} = -\,u_n\chi_C. \tag{20c}$$

By analysis of the steady state of the flow dominated system (20), one can the fixed point χ_{ss} which is located at $(\chi_A, \chi_B, \chi_C)_{ss} = (1, 0, 0)$. The phase portrait of the system (figure 7) shows trajectories following straight lines to the fixed point. These trajectories are described by the lines:

$$\frac{\chi_B}{1-\chi_A} = \text{constant} \tag{21}$$

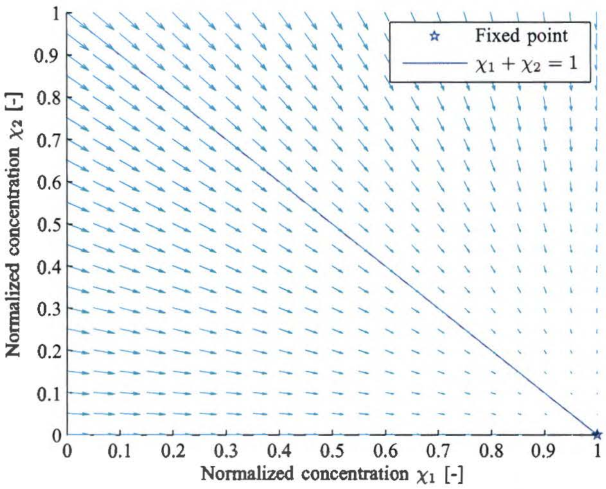


Fig. 7: Phase portrait of flow dominated system, described by equations (20) and the parameters given in table II.

The time solution for the first order system described by the equations (20) is given by equations (22). In these equations the values χ_{A1} and χ_{B1} are the initial conditions at the beginning of the cold period.

$$\chi_A(\tau) = (\chi_{A1} - 1)e^{-u_n\tau} + 1 \tag{22a}$$

$$\chi_B(\tau) = \chi_{B1}e^{-u_n\tau} \tag{22b}$$

Fixed point analysis of the reaction dominated system (19) reveals that the fixed point χ_{ss} is located at $(\chi_A, \chi_B, \chi_C)_{ss} = (0, 0, 1)$. The phase portrait (figure 8) shows a nullcline for $\frac{d\chi_2}{dt} = 0$, given by equation (23). For states above the nullcline the concentration χ_B decays as function of time.

$$\chi_B = \frac{1}{ky^{E-1}}\chi_A \tag{23}$$

Since the system described by the equations (19) is a linear system, the solution to the differential equations can be obtained by use of the forward and inverse Laplace transform. Using (χ_{A0}, χ_{B0}) as the initial conditions for χ_A and χ_B,

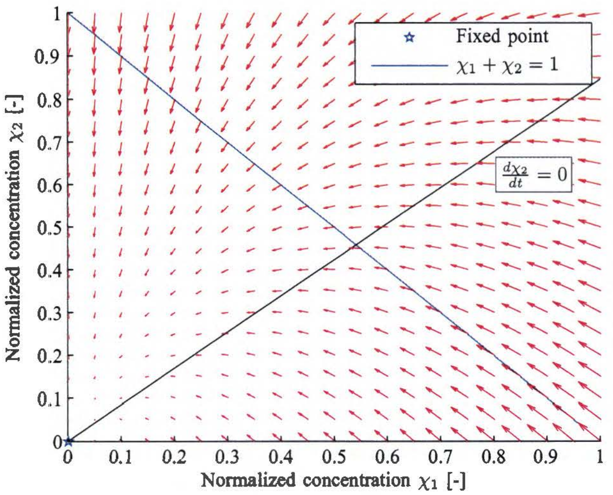


Fig. 8: Phase portrait of reaction dominated system, described by equations (19) and the parameters given in table II.

their respective time functions are given by the equations (24a) and (24b).

$$\chi_A(\tau) = e^{-y\tau}\chi_{A0} \tag{24a}$$

$$\chi_B(\tau) = \frac{1 + ky^{E-1}}{1 - ky^{2(E-1)}}\left(e^{-ky^E\tau} - e^{-y\tau}\right)\chi_{A0} + e^{-ky^E\tau}\chi_{B0} \tag{24b}$$

C. Periodic temperature switching

A system $\dot{x}(t) = f(x, u, t)$ is τ-periodic if $x(t) = x(t + \tau)$ for all t in $\mathbb{R}^+$. This implies that it must be possible to reach the initial conditions again after certain time. For the system under study this means that is must be possible reach the combination of concentrations where the reaction has started again. Because during the high temperature all trajectories lead to the fixed point $(0, 0, 1)$, this is only the case for start points χ_{10}, χ_{20} where the trajectory during the high temperature stays above the line which is describing the trajectories of the flow dominated system. More formal, inequality (25) holds in the starting points.

$$\left.\frac{\frac{d\chi_B}{dt}}{\frac{d\chi_A}{dt}}\right|_{T=T_{pulse}} > \left.\frac{\frac{d\chi_B}{dt}}{\frac{d\chi_A}{dt}}\right|_{T=T_{low}} \tag{25}$$

The phase planes of the reaction dominated and flow dominated system are combined in figure 9. The part of the state space where equation (25) holds is denoted as χ_{start} and is represented by the area under the line (26):

$$\left.\frac{\frac{d\chi_B}{dt}}{\frac{d\chi_A}{dt}}\right|_{T=T_{pulse}} = \left.\frac{\frac{d\chi_B}{dt}}{\frac{d\chi_A}{dt}}\right|_{T=T_{low}}, \tag{26}$$

which can be rewritten to:

$$\chi_B = \frac{\chi_A(1 - \chi_A)}{\chi_A + ky^{E-1}(1 - \chi_A)}. \tag{27}$$

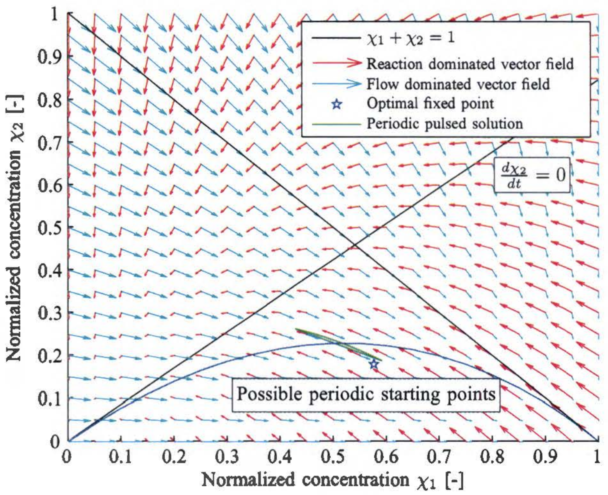


Fig. 9: Combined phase portraits of a system under periodic temperature switching. Please note: Because of the big variation in time constants in both systems, both vector fields have their own timescale and relation between length of vectors of not preserved in this figure.

Because the vectors of the flow and reacting are have opposite directions on line 26, this is also the line where the steady state solutions of a system operating at T_{high} lies on!

As already mentioned before, in order to operate periodically the trajectory of the reaction dominated system starting from (χ_{A0}, χ_{B0}) should intersect the trajectory of the flow dominated system which contains the point (χ_{A0}, χ_{B0}) at the point (χ_{A1}, χ_{B1}) (see figure 11 for visual representation). The time of intersection can be calculated for each starting point by the procedure given below.

In the point of intersection between the trajectory of the reaction dominated system and the trajectory of the flow dominated system containing the starting point, equation (28) is satisfied.

$$\frac{\chi_B(\tau)}{1 - \chi_A(\tau)} = \frac{\chi_{B0}}{1 - \chi_{A0}} \tag{28}$$

The value of τ for which this equation holds, is the time that the temperature is equal to T_{pulse}. Due to the transcendental nature of the problem, the time of intersection cannot be calculated analytically. Instead, it can be calculated by minimisation of the difference of the functions:

$$\tau_{high} = \arg\min_{\tau} \left\| \frac{\chi_B(\tau)}{1 - \chi_A(\tau)} - \frac{\chi_{B0}}{1 - \chi_{A0}} \right\|_2 \tag{29}$$

$$\text{subject to} \quad \tau > 0 \tag{30}$$

Once for a starting point in χ_{start} the time to reach the intersection is know, the point of intersection can be calculated. Subsequently, the yield resulting from this solution can be calculated by equation (9). The yield of the periodic solution for each starting point in χ_{start} is shown in figure 10. The starting point of the periodic trajectory which gives the maximum yield can be found by the optimization problem (31).

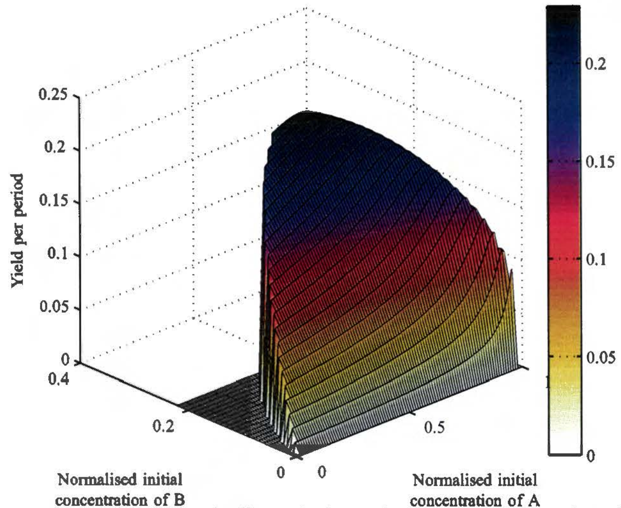


Fig. 10: Yield of periodic solutions for the starting points in χ_{start}.

$$\max \bar{Y}_B = \max_{\tau_1,\tau_2} \frac{1}{\tau_1+\tau_2}\left(\int_0^{\tau_1} u_n \chi_B(\tau)d\tau + \int_{\tau_1}^{\tau_2} u_n \chi_B(\tau)d\tau\right) \tag{31}$$

subject to:

$$\begin{array}{lcl} (\chi_{A0},\chi_{B0}) & \in & \chi_{start} \\ \tau_{pulse_{min}} & < \tau_1 < & \tau_{pulse_{max}} \\ \tau_{low_{min}} & < \tau_2 < & \tau_{low_{max}} \end{array}$$

for $0 < \tau < \tau_1$

$$\begin{array}{rcl} \chi_B(\tau) & = & \frac{1+ky^{E-1}}{1-ky^{2(E-1)}}\left(e^{-ky^E\tau} - e^{-y\tau}\right)\chi_{A0} \\ & & +e^{-ky^E\tau}\chi_{B0} \end{array}$$

for $\tau_1 < \tau < \tau_2$

$$\chi_B(\tau) = \chi_{B1}e^{-u_n\tau}$$

From figure 10 and numerical optimization it seems that the maximum yield is achieved if the point (χ_{A0},χ_{B0}) is chosen such that χ_2 is maximal. This it remarkable because this point is also the optimal steady state with respect to the selectivity of the system operating at T_{high} and the flow chosen according to (15). Unfortunately, a proof cannot be given because the point (χ_{A1},χ_{B1}) cannot be expressed analytically due to the transcendental nature of equation (26).

The numerical algorithm has been applied to a system with the parameters shown in table II, and the constraint of a minimum pulse time of 5 seconds. The solution is compared with a system operating at a steady temperature of $430K$ and $u_n = \hat{u}_n$. The optimal periodic solution and steady state solution with maximum average concentration is shown in figure 11. The concentration of χ_2 in steady state solution is 0.18. The periodic temperature switched system has an average solution χ_2 of 0.22, which is an increase of 22% with respect to steady state operation.

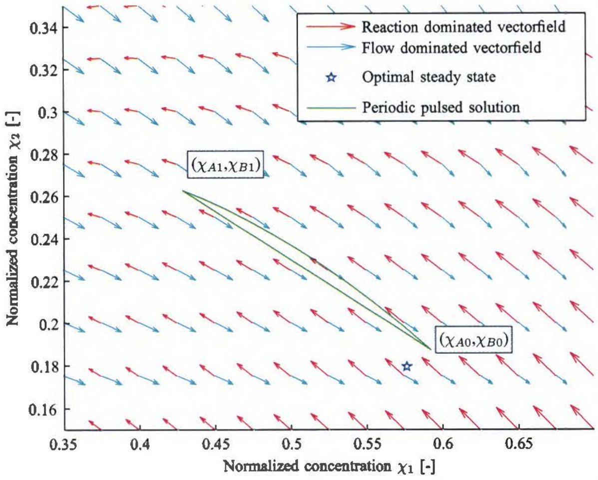


Fig. 11: Optimal periodic solution for a minimal pulse duration of 5 seconds. Reaction and system parameters are shown in table II

V. EFFECT OF NON-UNIFORM ENERGY DISTRIBUTION

The main argument to research the perspectives of non-uniform heating lies in the expectation that by non-uniform heating fast dynamic behavior can be created. In this section, the relation between the dimensions of a non-uniform heated system and its dynamic behavior will be investigated.

The amount of material that reacts as the result of the non-uniform supply of a given amount of energy, depends on the temperature increase, the volume that is heated and time that it takes for a temperature profile to distribute over the total medium.

The effect of nonuniform energy distribution on a chemical reacting system has been investigated for a spherical geometry, which centre is heated by a pulse of thermal energy. The relation between the diameter of the heated centre and the dynamics behavior has been studied.

In this section it is assumed that thermal diffusion dominates the dynamics behavior of the system. It is assumed that the enthalpy change by the reaction in the system is small with respect to the heat capacity ($\Delta H \approx 0$) and that the material diffusivity is small compared to the thermal diffusivity ($D_C \approx 0$). Under these assumptions, the coupling between the equations (3) is broken down. Under these assumptions the temperature distribution can be modelled by the independent equation:

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T + \frac{u_{ext}}{\rho c_p} \tag{32}$$

where u_{ext} is the external power input to the system.

The reacting system is studied on a spherical coordinate system, where symmetries with respect to θ and ϕ is assumed. By defining u_{ext}, heat is applied to a sphere with radius a in the center of spherical system. Mathematically, the pulse is described by the equation:

$$u_{ext} = \frac{3Q}{4\pi a^3}4\pi r^2\delta(t)(1-\epsilon(a-r)), \tag{33}$$

such that the energy is distributed equally over the volume in the sphere with radius a. In the function δ represents the Dirac delta and ϵ denotes the Heaviside step function. Application of this input function to equation (32) can be modelled as an initial value problem, with the initial conditions:

$$T(r,0) = \begin{cases} T_0 + T_p & \text{for } 0 < \text{r} < \text{a}, \\ T_0 & \text{for r} \geq \text{a} \end{cases} \tag{34}$$

As a result of the spherical coordinate system, the boundary condition:

$$\frac{\partial T(0,t)}{\partial r} = 0,$$

has to be applied.

The difference in temperature with respect to the environmental temperature T_0 is defined as T_d such that:

$$T(r,t) = T_0 + T_d(r,t). \tag{35}$$

The solution for the transient temperature profile resulting from the initial conditions (34) can be calculated analytically [31] and is given by the equation:

$$\begin{aligned} T_d(r,t) = &\frac{T_p}{2}\left(\operatorname{erf}\frac{a+r}{2\sqrt{D_T t}} + \operatorname{erf}\frac{a-r}{2\sqrt{D_T t}}\right) + \frac{T_p}{r}\sqrt{\frac{D_T t}{\pi}} \\ &\left(\exp\left(-\frac{(a-r)^2}{4D_T t}\right) - \exp\left(-\frac{(a+r)^2}{4D_T t}\right)\right) \end{aligned} \tag{36}$$

where:

$$\operatorname{erf} z = \frac{2}{\sqrt{\pi}}\int_0^z \exp\left(-\eta^2\right) d\eta. \tag{37}$$

An example of the temperature profile for $a = 1 \cdot 10^{-3}$m at several time intervals is shown in figure 12

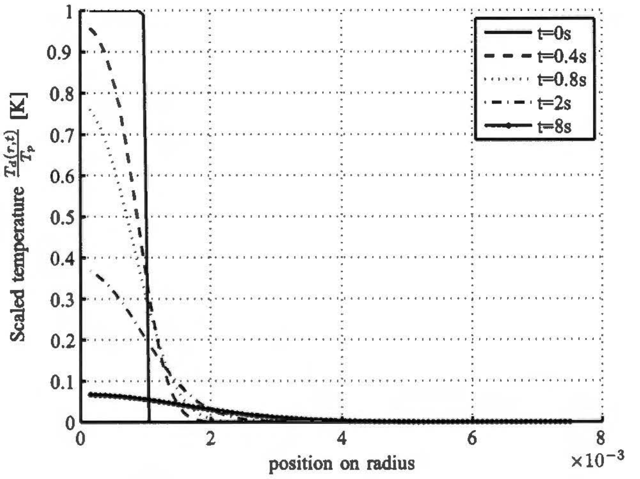


Fig. 12: Temperature profile for $a = 1 \cdot 10^{-3}$m as function of time. Simulation parameters in table III.

By analysis of this equation, it is made clear that fast dynamic behavior can be created by non uniform heating. If one defines r as $r = \beta a$ where $\beta \in \mathbb{R}^+$, relation (36) can be rewritten to:

$$\begin{aligned} T_d(r,t) = &\frac{T_p}{2}\left(\operatorname{erf}\frac{1+\beta}{2\sqrt{D_T\frac{t}{a^2}}} + \operatorname{erf}\frac{1-\beta}{2\sqrt{D_T\frac{t}{a^2}}}\right) + \\ &\frac{T_p}{\beta}\sqrt{\frac{D_T\frac{t}{a^2}}{\pi}}\left(\exp\left(-\frac{(1-\beta)^2}{4D_T\frac{t}{a^2}}\right) - \exp\left(-\frac{(1+\beta)^2}{4D_T\frac{t}{a^2}}\right)\right) \end{aligned} \tag{38}$$

From equation (38) it follows that scaling of dimensions of system by α has the same effect as scaling of the time axis or D_T by α^2. It can be concluded that fast dynamics can be realised by choosing a small value for a.

By decreasing the value of a, also the volume of the heated sphere is decreased. Furthermore, the temperature rise as result of an energy pulse is increased. The effect of change of a on the amount of converted material will be studied next. It it is assumed that in the medium, the first order reaction from a reactant A to a product B (mechanism 39) takes place.

$$A \quad \xrightarrow{k_1} \quad B \tag{39}$$

The concentration change as a result of this reaction is described by the equations 40.

$$\frac{\partial C_A}{\partial t} = -\, C_A R(T(r,t)) \tag{40a}$$

$$\frac{\partial C_B}{\partial t} = +\, C_A R(T(r,t)) \tag{40b}$$

where R is the relation between temperature and reaction rate according (1).

The initial conditions and boundary conditions used in this problem are:

$$\begin{aligned} C_A(r,0) =& C_{A0}, & \frac{\partial C_B(0,t)}{\partial r} &= 0, \\ C_B(r,0) =& 0, & \frac{\partial C_A(0,t)}{\partial r} &= 0. \end{aligned}$$

The differential equation describing the change of concentration, can be solved by means of separation of variables. The solution is given by equation (41),

$$\int_{C_A(r,0)}^{C_A(r,t)} \frac{dC_A(r,t)}{C_A(r,t)} = \int_0^t -R(T(r,\tau))d\tau \tag{41}$$

Such that the concentration B at position r and time t can be calculated by use of the equations:

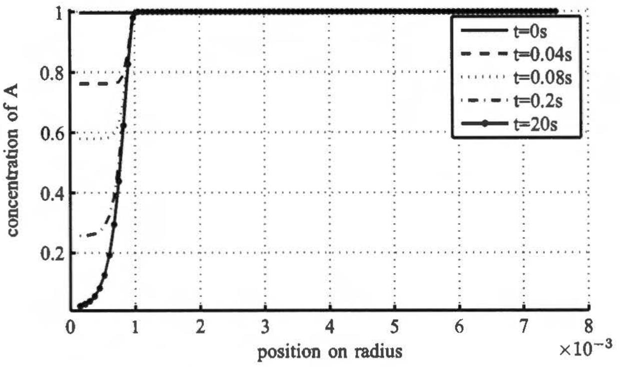
$$C_A(r,t) = C_A(r,0)\exp\int_0^t -R(T(r,t))d\tau \tag{42}$$

$$C_B(r,t) = C_A(r,0)\left(1 - \exp\int_0^t -R(T(r,t))d\tau\right) \tag{43}$$

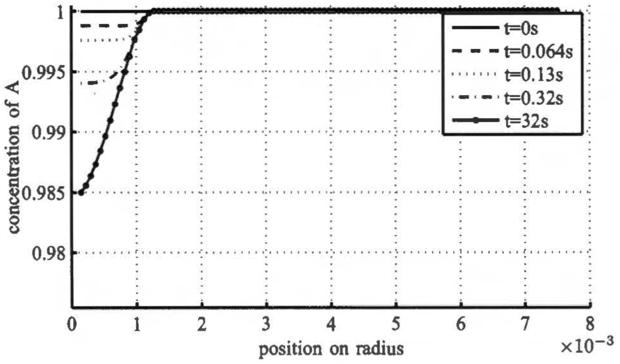
In the end, the mass of converted product B can be calculated by integration over entire sphere:

$$M_B(t) = \int_0^\infty r^2 C_B(r,t)dr. \tag{44}$$

For numerical calculation the infinite medium is truncated at $r = g$. The consistency of the calculation is preserved if the



(a) Heated sphere with radius $1 \cdot 10^{-3}$ m.



(b) Heated sphere with radius $1.26 \cdot 10^{-3}$ m.

Fig. 13: Concentration of species A as function of time after supply of energy pulse. In the simulations $\epsilon = 5 \cdot 10^{-4}$ was used.

total amount of energy is conserved in the time interval of study, such that:

$$Q(0) - Q(t) = Q(0) - \rho c_p \int_0^g r^2 T(r,t) dr < \epsilon. \qquad (45)$$

The concentration change for cases with different radii and a constant amount of energy have been investigated. Several simulations have been setup with the parameters given in table III. In figure 13 the time varying concentration as result of an energy pulse with $Q = 15$J is shown. The volume of the heated region in case 1 is chosen half of the volume in case 2. In case 1 the value a=$1 \cdot 10^{-3}$m is used, while in case 2 $a = \sqrt[3]{2} \cdot 10^{-3}$m is used. From the figures it follows that the change of concentration change due to an energy pulse depends heavily on the radius of the heated sphere. The figures show that the volume over which energy is distributed has a large impact on the total amount of material that will be converted before the energy has been spread out over the medium.

VI. Conclusion

In section III, a first principles model for the interaction of a catalyst with its environment has been presented. With use of this model it has been shown that the selectivity of the presented reaction can be influenced by selective and unsteady heating of the direct environment of the catalyst. Furthermore, it has been shown that by use of selective heating a higher reaction rate with respect to a specific product can be realised than by uniform heating at equal bulk temperatures.

In section IV, it has been shown that by variation of the temperature over time, the average concentration of the intermediate product in a consecutive reaction mechanism can be increased beyond values that can be obtained at steady state. A numerical algorithm for the maximal achievable yield is given. It can be concluded that by unsteady operation selectivity of reactions can be influenced and increased.

In section V the effect of scaling of the dimensions of a spherical system on its dynamic behaviour has been investigated. By decreasing the radius of the heated center in a reacting system, fast dynamic behaviour can be realised. It has been shown that the volume if the sphere over which energy is distributed has a large impact on the reaction that will occur and on the total amount of material that will be converted before the energy is spread out over the medium.

The models show that pulsed non-uniform heating of catalysts is an interesting idea and that it can have big advantages for the application of control in chemical reactions. By non-uniform heating fast dynamic behavior can be realised, selectivity can be influenced and bulk reactions can be reduced. More research on non-uniform unsteady heating in chemical systems is needed. The developed models have to be applied to real reaction and have to be verified with experiments and measurements. A laboratory setup has to be developed to show a proof of concept.

VII. Future Research

Where needed the presented models have to be made more precise. The interaction between transport mechanisms and chemical reactions should be researched in more detail. The potential of non-uniform pulsed heating for the control of polymerisation reaction should be investigated, because it is known that transport mechanisms play a large role in this class for reaction mechanisms. Furthermore, chemical parameters valid in wide ranges of concentration and temperature have to be measured, such that they can be applied to dynamic models.

Also some more fundamental research has to be done. In the derivation of the Arrhenius equation, the Boltzmann distribution of the molecule velocities is used. The derivation of Boltzmann distribution relies on the assumptions that a system is in thermodynamic equilibrium and that the probability to be at a certain state is equal for all molecules in the system. One has to reconsider this assumptions when large gradients in thermodynamic states are realised. Therefor, the validity of the Arrhenius equation for non-uniform heated systems has to be researched.

VIII. Acknowledgements

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APPENDIX A
LIST OF SYMBOLS

Symbol:		Description:	Unit:
ϕ	=	Material flow	$m^3 \cdot s^{-1}$
ρ	=	Specific density	$kg \cdot m^{-3}$
τ	=	Dimensionless time	–
χ_i	=	Normalised concentration	–
a	=	Velocity	$m \cdot s^{-1}$
c_p	=	Specific heat capacity	$J \cdot kg^{-1} K^{-1}$
f_i	=	Function depending on reaction	–
k	=	Frequency factor ratio	–
k_i	=	Frequency factor	s^{-1}
r_i	=	Reaction rate for step i	variable
u_n	=	Normalised flow	–
q_i	=	Power flow	W
C_i	=	Concentration of species i	$mol \cdot m^{-3}$
D_T	=	Thermal diffusion coefficient	$m^2 \cdot s^{-1}$
D_C	=	Material diffusion coefficient	$m^2 \cdot s^{-1}$
E	=	Dimensionless activation energy	–
E_i	=	Activation energy for reaction step i	$J \cdot mol^{-1}$
ΔH_i	=	Enthalpy change in reaction step i	$J \cdot mol^{-1}$
N	=	Site concentration	$mol \cdot m^{-3}$
R_g	=	Gas constant	$J \cdot K^{-1} mol^{-1}$
S_i	=	Selectivity with respect to species i	–
T	=	Temperature	K
T_n	=	Dimensionless temperature	–
V	=	Volume	m^3
Y_i	=	Yield of species i	mol

APPENDIX B
DYNAMICS OF CSTR WITH CONSECUTIVE REACTION

The dynamics of a CSTR in which the consecutive reaction 6 is carried out, are described by equations (46).

$$\frac{dC_A}{dt} = \frac{\phi(t)}{V}\left(C_{A0} - C_A\right) - C_A R_1 \tag{46a}$$

$$\frac{dC_B}{dt} = \frac{\phi(t)}{V}\left(C_{B0} - C_B\right) + C_A R_1 - C_B R_2 \tag{46b}$$

$$\frac{dC_C}{dt} = \frac{\phi(t)}{V}\left(C_{C0} - C_C\right) + C_B R_2 \tag{46c}$$

These equations are rewritten in dimensionless form (equations (7)) using the dimensionless numbers and identities:

$$\tau = k_1 t, \qquad T_n = \frac{TR}{E_1}, \qquad y = e^{-1/T_n},$$
$$k = \frac{k_2}{k_1}, \qquad E = \frac{E_2}{E_1}, \qquad u_n = \frac{\phi}{V k_1},$$
$$\chi_1 = \frac{C_A}{C_{A0}}, \qquad \chi_2 = \frac{C_B}{C_{A0}}, \qquad \chi_3 = \frac{C_C}{C_{A0}}.$$

APPENDIX C
DYNAMICS FOR OF NON-UNIFORM MODEL

The dynamics of bulk in the non-uniform reactor model are described by the equations:

$$\frac{dC_{A_B}}{dt} = \frac{\phi_C}{V_B}(C_{A_C} - C_{A_B}) + \frac{\phi_F}{V_B}(C_{A_0} - C_{A_B}) - C_{A_B} k_1^+(T_B) \tag{47a}$$

$$\frac{dC_{B_B}}{dt} = \frac{\phi_C}{V_B}(C_{B_C} - C_{B_B}) + \frac{\phi_F}{V_B}(C_{B_0} - C_{B_B}) \tag{47b}$$

$$\frac{dC_{C_B}}{dt} = \frac{\phi_C}{V_B}(C_{C_C} - C_{C_B}) + \frac{\phi_F}{V_B}(C_{C_0} - C_{C_B}) + C_{A_B} k_1^+(T_B) \tag{47c}$$

$$\frac{dC_{D_B}}{dt} = \frac{\phi_C}{V_B}(C_{D_C} - C_{D_B}) + \frac{\phi_F}{V_B}(C_{D_0} - C_{D_B}) \tag{47d}$$

$$\frac{dT_B}{dt} = \frac{\phi_C}{V_B}(T_C - T_B) + \frac{\phi_F}{V_B}(T_0 - T_B) \tag{47e}$$

The dynamics in the direct vicinity of the catalyst in the non-uniform reactor model are described by the equations:

$$\frac{dC_{A_C}}{dt} = \frac{\phi_C}{V_C}(C_{A_B} - C_{A_C}) - C_{A_C} k_1^+(T_C) - C_{A_C} C_* k_2^+(T_C) + C_{A^*} k_2^-(T_C) \tag{48a}$$

$$\frac{dC_{B_C}}{dt} = \frac{\phi_C}{V_C}(C_{B_B} - C_{B_C}) - C_{B_C} C_* k_3^+(T_C) + C_{B^*} k_3^-(T_C) \tag{48b}$$

$$\frac{dC_{A^*}}{dt} = C_{A_C} C_* k_2^+(T_C) - C_{A^*} k_2^-(T_C) - C_{A^*} C_{B^*} k_4^+(T_C) \tag{48c}$$

$$\frac{dC_{B^*}}{dt} = C_{B_C} C_* k_3^+(T_C) - C_{B^*} k_3^-(T_C) - C_{A^*} C_{B^*} k_4^+(T_C) \tag{48d}$$

$$\frac{dC_{C_C}}{dt} = \frac{\phi_C}{V_C}(C_{C_B} - C_{C_C}) + C_{A_C} k_1^+(T_C) \tag{48e}$$

$$\frac{dC_{D_C}}{dt} = \frac{\phi_C}{V_C}(C_{D_B} - C_{D_C}) + C_{A^*} C_{B^*} k_4^+(T_C) \tag{48f}$$

$$\frac{dT_C}{dt} = \frac{\phi_C}{V_C}(T_R - T_C) + \frac{1}{\rho C_p V_C} q_{in} \tag{48g}$$

$$N = C_* + C_{A^*} + C_{B^*} \tag{48h}$$

where * denotes a free site at the catalyst.

APPENDIX D
SIMULATION PARAMETERS

TABLE I: Model parameters used for section III

Parameter:	Value:	Unit:	
k_0	$2 \cdot 10^7$	s^{-1}	
E_0	$7 \cdot 10^4$	$\mathrm{J \cdot mol^{-1}}$	
k_1	$0.1k_0$	$\mathrm{mol \cdot m^{-3}s^{-1}}$	
E_1	$0.8E_0$	$\mathrm{J \cdot mol^{-1}}$	
$k_i^{\pm}$	$0.01k_0$	$\mathrm{mol \cdot m^{-3}s^{-1}}$	for $\mathrm{i} = [2,3]$
$E_i^{\pm}$	$0.8E_0$	$\mathrm{J \cdot mol^{-1}}$	
k_4	$0.01k_0$	$\mathrm{mol \cdot m^{-3}s^{-1}}$	
E_4	E_0	$\mathrm{J \cdot mol^{-1}}$	
C_{A0}	1.2	$\mathrm{mol \cdot m^{-3}}$	
C_{B0}	1.0	$\mathrm{mol \cdot m^{-3}}$	
T_0	273	K	
N	1	$\mathrm{mol \cdot m^{-3}}$	
V_C	$1 \cdot 10^{-8}$	$\mathrm{m^3}$	
V_R	$1 \cdot 10^{-6}$	$\mathrm{m^3}$	
ϕ_f	$1 \cdot 10^{-7}$	$\mathrm{m^3 \cdot s^{-1}}$	
ϕ_C	$1 \cdot 10^{-7}$	$\mathrm{m^3 \cdot s^{-1}}$	

TABLE II: Model parameters used for section IV

Parameter:	Value:	Unit:
E_1	$3.48 \cdot 10^4$	$\mathrm{J \cdot mol^{-1}}$
E_2	$0.9 \cdot E_1$	$\mathrm{J \cdot mol^{-1}}$
k_1	12	s^{-1}
k_2	$0.7 \cdot k_1$	s^{-1}
A_0	$6 \cdot 10^3$	$\mathrm{mol \cdot m^{-3}}$
T_{ss}	430	K
T_{min}	300	K
T_{max}	1000	K
Dimensionless parameters:		
k	0.7	[–]
E	0.9	[–]

TABLE III: Model parameters used for section V

Parameter:	Value:	Unit:
T_0	270	K
c_p	$4.1480 \cdot 10^3$	$\mathrm{J \cdot kg^{-1}K^{-1}}$
α	0.6	$\mathrm{W \cdot m^{-1}K^{-1}}$
ρ	998	$\mathrm{kg \cdot m^{-1}}$
D_T	0.5	$\mathrm{m^2 \cdot s^{-1}}$
E	$9 \cdot 10^4$	$\mathrm{J \cdot mol^{-1}}$
k	$1 \cdot 10^5$	s^{-1}

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