Abstract

The reverse flow reactor (RFR) is an important member of the class of unsteady state reactors. The imposed flow-reversal induces characteristic dynamics during the course of a switching cycle. High temperature catalytic reactions exhibit a complex behavior since the high temperature level modifies reaction yield as well as the selectivity and opens up additional reaction pathways such as homogenous reactions. The combination of a reverse flow reactor with a high temperature catalysis provides an interesting system to investigate in. The chemical-thermal coupling-mechanisms in the high temperature domain are still poorly understood and efficient modeling as well as simulation specifically of the periodicity is by no means standard procedure. The investigation of both the dynamic behavior and the cyclic steady state display a promising way of obtaining insights into the reaction on a microscopic scale from macroscopic observation. The decomposition of N_2O in a reverse-flow-reactor is considered as an example. Appropriate mathematical algorithms for efficiently treating the equation, parameter studies and an interesting analogy to a loop reactor with parallel reactions are presented. The algorithms used are qualitatively superior to those previously published to calculate cyclic steady states.

1 Introduction

Reaction kinetics are crucial when planning and designing a new process. One can either measure the (macro)kinetics of the reaction system being considered or derive an expression on the basis of the underlying elementary reaction microkinetics. The macrokinetic relationship is the basis for further modelling and simulations steps in process design. In general, it is not possible to resolve details of kinetic behaviour from the macroscopic perspective (cf. Figure 1). Furthermore, experimental kinetics may only be employed reliably in the vicinity of the measured paramters; extrapolation to other conditions is fraught with uncertainity. Processes operated in unsteady-state are a fertile field of research since the complex transient behaviour sometimes provides a much greater amount of exploitable information than steady-state conditions. This is why unsteady-state processes have recently attracted attention as a means for enhancing our understanding of the interdependency of observed macroscopic behaviour and individual microscopic processes. For the case of two parallel reactions in a circulation loop reactor Mangold et. al. [3] found that under certain conditions the propagation velocity of the temperature front(s) and the difference between the two activation energies are intimately connected. In their work, the numerical analysis of ignition-extinction bifurcations becomes the key to understanding the complex non-linear behaviour of the system. The investigation of N_2O decomposition in a reverse flow reactor (RFR) presented in this paper is in many respects analogous.

Figure 1: Course of Process design

1.1 Hybrid N_2O decomposition

In contrast to normal catalytic processes, high temperature catalysis can exhibit addtional unwanted or desirable homogeneous (parallel) reactions. Such behaviour is referred to as catalytically promoted homogeneous reaction or simply hybrid reaction. Homogenous reaction can be induced by a

temperature rise in the boundary layer at the catalytic surface. The decompostion N_2O in the high temperature domain offers the possibility of investigating coupling mechanisms of hybrid reactions for a fairly simple reaction system (see Figure 2). Furthermore, the destruction of the 'greenhouse gas' N_2O is of practical relevance due to its negative environmental impact.
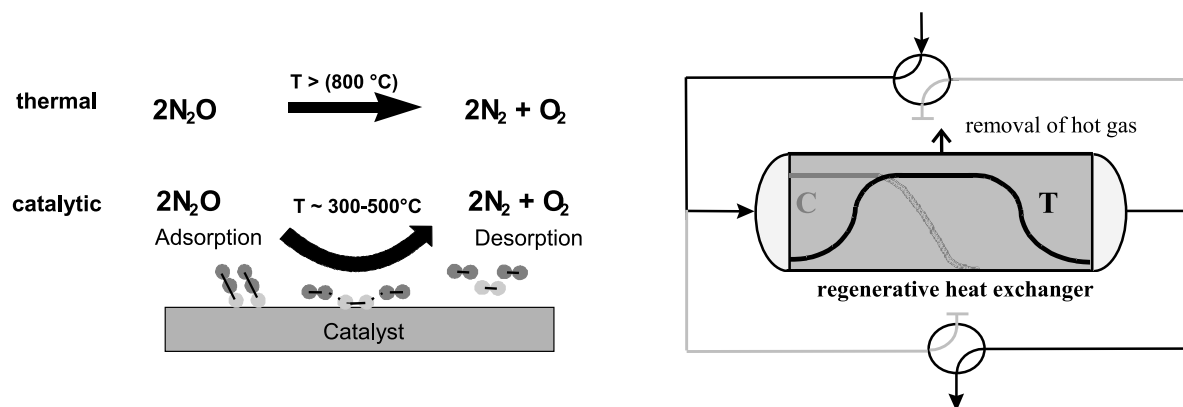

Figure 2: Reaction Pathways and Schematic of RFR

1.2   Reverse Flow Reactor

The reverse flow reactor is an important type of unsteady-state reactor, often exhibiting lower energy requirements and more stable operating behaviour than its steady-state equivalent. The flow reversal imposed induces characteristic reactor dynamics during the course of a switching cycle. In this work these reactor dynamics and the elegant decoupling of concentration and thermal fronts are proposed as a means of discriminating qualitatively and unequivocally between alternative kinetic mechanisms.

2   Modelling

2.1   Reactor Model

In this work we apply a one-dimensional pseudohomogeneous model. The model accounts for heat loss, which is critical in the high temperature domain, and assumes that all physical properties are are independent of temperature T and concentration C. A more detailed description of the model equations can be found in [10]. The model is comprised of the following two partial differential equations describing mass and energy balances:

3

$$0 \;=\; D_{\text{eff}} \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - r_{\text{ges}}(T, C) \tag{1}$$

$$(1 - \varepsilon)(\varrho\, c_P)_s \frac{\partial T}{\partial t} \;=\; \lambda_{\text{eff}} \frac{\partial^2 T}{\partial z^2} - (\varrho\, c_P)_g v \frac{\partial T}{\partial z} + \frac{k}{r}(T - T^{\text{amb}}) + (-\Delta H_r) r_{\text{ges}}(T, C) \tag{2}$$

2.2 Kinetical Aspects - TC and TCC Model

Both the heterogeneous and homogeneous reaction can be regarded as first order with respect to the N_2O concentration. The decomposition is exothermic, irreversible and Arrhenius terms account for the temperature dependence of each reaction pathway. The limiting influence of the mass transport through the boundary layer is also implemented in the kinetics of the heterogeneous reaction (see (3)). The constants used in the simulations are listed below:

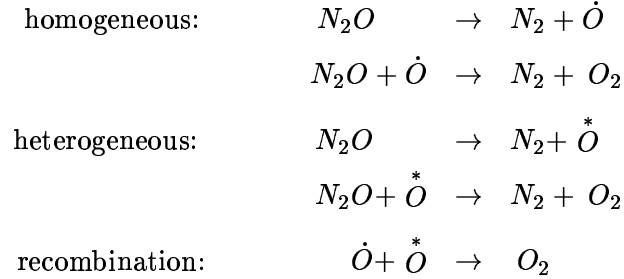| Symbol	Value	Units
k^0_{hom}	$4.4E11$	$[1/s]$
$E_{a\text{hom}}$	$2.5E5$	$[J/mol]$
k^0_{het}	$2.5E8$	$[1/s]$
$E_{a\text{het}}$	$1.5E5$	$[J/mol]$
$(-\Delta H_r)$	81600	$[J/mol]$

TC-Model

The TC-model (thermal coupling) regards to two reaction pathways as being chemically independent of one another so that the overall reaction rate is simply the sum of the two contributions (see (3)).

$$\text{homogeneous:} \qquad N_2O \;\rightarrow\; N_2 + 1/2\, O_2$$

$$\text{heterogeneous:} \qquad N_2O \;\rightarrow\; N_2 + 1/2\, O_2$$

$$r_{\text{ges}}^{\text{TC}}(T, C) = \left[\frac{a_v \cdot \beta \cdot k_{\text{het}}(T)}{a_v \cdot \beta + k_{\text{het}}(T)} + k_{\text{hom}}(T) \right] \cdot C \tag{3}$$

4

The TCC-(thermal-chemical coupling) model is comprised of a simple two-step mechanism for both individual, i.e. homo- and heterogeneous, reaction pathways. The recombination of oxygen represents the sole chemical coupling mechanism considered in this model. It should be stressed that there is no definitive verification for this model. Further information can be found in [2]. The reaction rate equation can be reduced to that of the TC-model augmented by a single correction term.

$$
\begin{aligned}
\text{homogeneous:} \quad & N_2O && \rightarrow && N_2 + \dot{O} \\
& N_2O + \dot{O} && \rightarrow && N_2 + O_2 \\
\text{heterogeneous:} \quad & N_2O && \rightarrow && N_2 + \overset{*}{O} \\
& N_2O + \overset{*}{O} && \rightarrow && N_2 + O_2 \\
\text{recombination:} \quad & \dot{O} + \overset{*}{O} && \rightarrow && O_2
\end{aligned}
$$

The intensity of recombination can be controlled by adjusting the parameter γ. The TC and TCC models are consistent, since for $\gamma = 0$ they become identical.

$$
r_{\text{ges}}^{\text{TCC}}(T,C) = r_{\text{ges}}^{\text{TC}}(T,C) - \gamma \cdot min(r_{\text{het}}, r_{\text{hom}}) \tag{4}
$$

3 Direct Calculation

It is known that for cylic steady-states the profiles upon sucessive flow reversals are mirror images of one another.

$$
T(z, t = 0) = T(L - z, t = \Delta t) \tag{5}
$$

Cyclic steady-states can be calculated by asymptotic **dynamic simulation** over numerous cycle until (5) is fullfilled, often a very time-consuming approach. The method of **direct calculation** is faster but much more challenging, since there is no commerical software available for this purpose. In this work we applied space-time finite-difference discretisation of the space-time domain [5, 6] similar to those proposed by Salinger and Eigenberger [7, 8] as basis for a Direct Algorithm. Alternatively one can apply shooting methods [9, 10]. Furthermore, UMFPACK subroutines were used

for efficiently solving the linear equations [1]. From this steady-state formulation well-established bifurcation analysis techniques can be used to investigate the influence of key parameters for instance [11]. In the case of ignition-extinction bifurcation analysis the feed concentration C^0 is a crucial parameter. Direct Algorithms offer the following advantages:

- Investigation of parameter sensitivity over a wide range

- Calculation of both stable und unstable periodic steady-states

- Rapid calculation of an entire solution trajectory

4 Results

A simple ignition-extinction bifurcation for q parallel reactions is comprised of a maximum of $2q + 1$ branches, $q + 1$ of which represent stable steady- states. Steady and unsteady branches alternate, as do the ignition and extinction points. Each trajectory starts with a stable (extinguished) solution branch (see Figure 3). Tracking the two possible extinction points with various activation energies for the heterogeneous reaction whilst maintaining the activation energy for the homogeneous reaction constant, lead to a (degenerated) pitchfork bifurcation (see Figure 4). This behaviour is completely analogous to that found in the circulation loop reactor mentioned above.
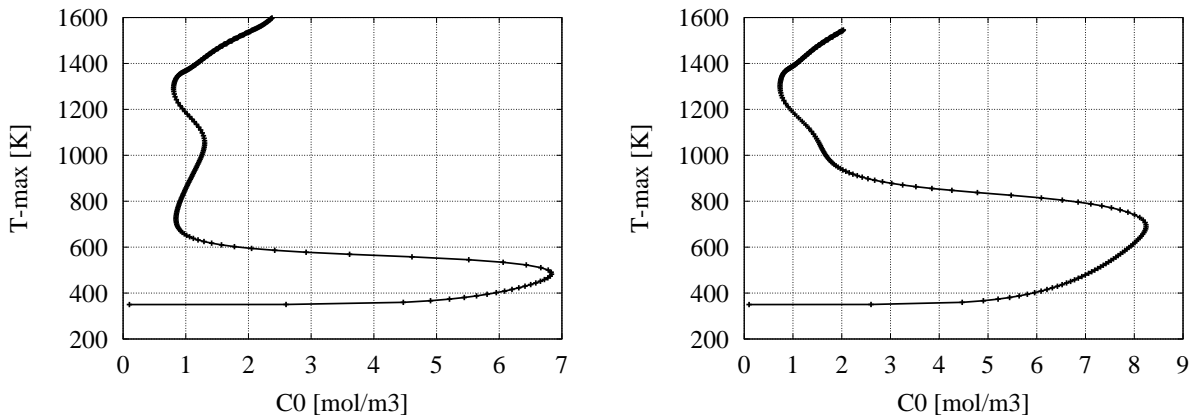

Figure 3: Simple ignition-extinction bifurcations for different activation energy of heterogeneous reaction (left: 100 KJ/mol, right: 140 KJ/mol)

For ignition-extinction bifurcations left of the splitting point in Figure ?? virtually no difference can be found between to results of the TC and TCC model.
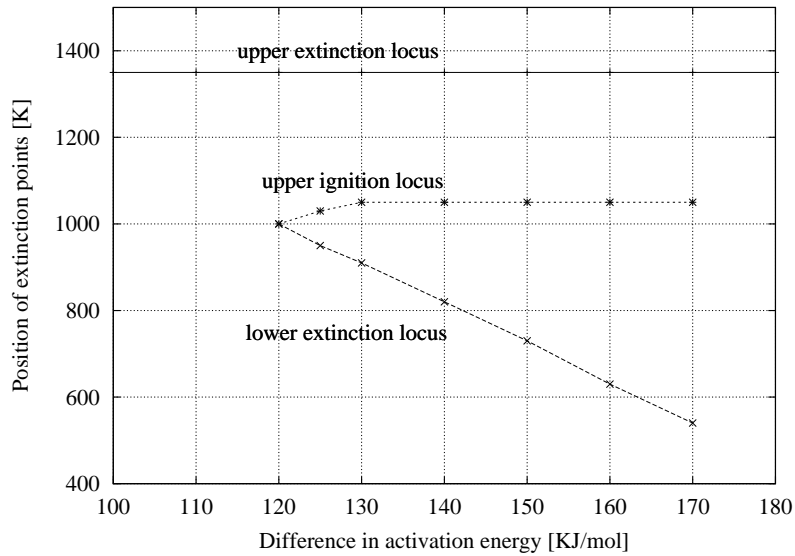
6

Figure 4: Degenerated pitchfork bifurcation of an RFR withs hybride N_2O decomposition

For bifurcations diagrams right to the splitting point the difference in applying TC or TCC model is quite obvious:

$$E_{\text{het}}^{A} = 120\frac{kJ}{mol}, \qquad a_v = 10\frac{1}{m}$$

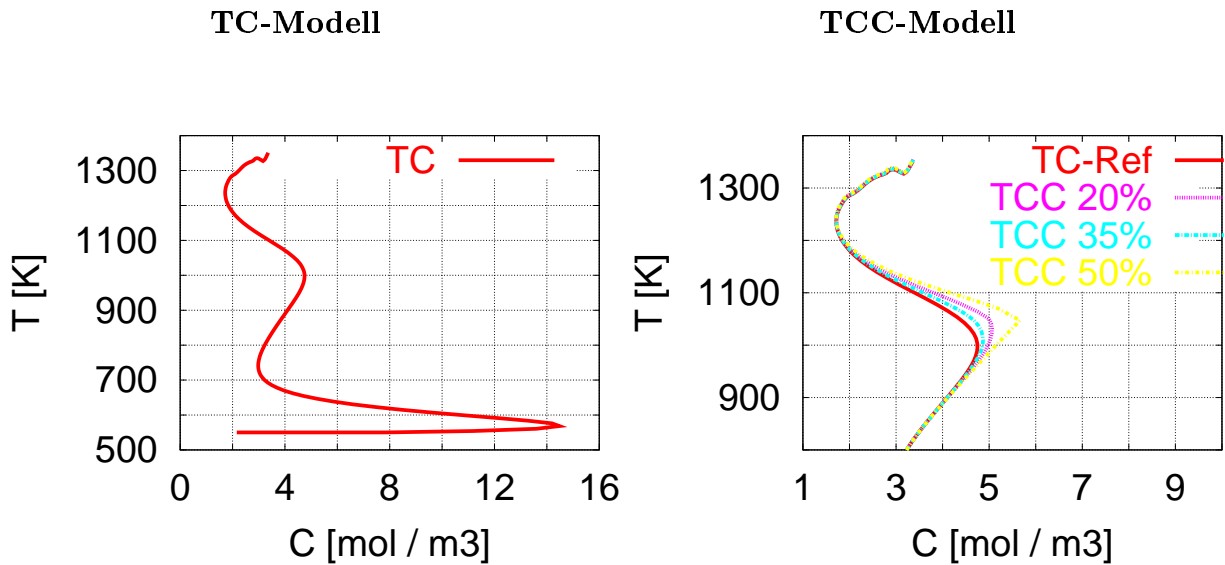**TC-Modell**   **TCC-Modell**

Figure 5: Significant influence of TC and TCC model for varying degree of chemical coupling, e.g. oxygen recombination ($\gamma = 20$, 35 or 50 %)

- Temperaturwindow of the suggested catalyst is too narrow

- Proposed TCC-Mechanismus exhibibits different macroskopic behaviour

- Is the different macroskopic behaviour measurable?

5 Outlook

We have shown that numerical bifurcation analysis is a powerful tool for investigating the complex nonlinear behaviour of the RFR. But there is still work left to do on several fields.
Modelling:

- Two-phase model for accounting difference in Temperature between gas and solid phase

- More detailed Kinetics

Numerical Analysis:

- Applying FEM packages and non-cartesian grid

- Non cartesian grid and adaptivity for treating steep fronts

- High performing computing, e.q. implementing efficient linear solvers

Experimental Analysis:

- Finding an more active and temperature resitent catalyst

References

[1] Davis, T.A., Duff, I.S., (1997), *A Combined Unifrontal/Multifrontal Method for unsymmetric Sparse Matrices*, Technical Report TR-97-016, Computer and Information Science and Engineering Department, University of Florida

[2] Galle, M., (2001) Thermal N_2O decomposition in regenerative heat exchanger reactors, *Chem. Eng. Sci.* **56**, No.4, 1587-1595

[3] Mangold, M., Kienle, A., Gilles, E.D., Richter, M. Roschka, E., (1999) Coupled reaction zones in a circulation loop reactor *Chem. Eng. Sci.* **54**, p 2597-2607

[4] Nieken, U. (1993): Abluftreinigung in katalytischen Festbettreaktoren bei periodischer Strömungsumkehr. *PhD Theses, Uni-Stuttgart,*

[5] Platte, F., Fredebeul, C. (2000), Dynamische und stationäre Simulation des Reaktionsverhaltens eines Strömungsumkehrreaktors, *Ergebnisberichte Angewandte Mathematik Nr. 190 - T, Uni Dortmund*

[6] Platte, F., Fredebeul, C. (2001), Zur Anwendung direkter Löser bei der direkten Berechnung periodisch stationärer Zustände eines Strömungsumkehrreaktors, *Ergebnisberichte Angewandte Mathematik Nr. 197 - T, Uni Dortmund*

[7] Salinger, A.G. (1996): The Direct Calculation of Periodic States of the Reverse Flow Reactor - I. Methodology and Propane Combustion Results. *Chem. Eng. Sci.* **51**, 4903-4913.

[8] Salinger, A.G.,(1996), The Direct Calculation of Periodic States of the Reverse Flow Reactor - II. Multiplicity and Instabiliy. *Chem. Eng. Sci.* **51**, 4915-4922

[9] Khinast, U., Luss, D., (1997), Mapping Regions with Different Bifurcation Diagrams of a Reverse Flow Reactor. *A.I.Ch.E.J* **44**, 2034-2047

[10] Khinast, U., Gurumoorthly, A., Luss, D., (1997), Complex Dynamic feature of a cooled Reverse-Flow Reactor. *A.I.Ch.E.J* **44**, 1128-1140

[11] Seydel, R., 1990, Practical bifurcation and stability analysis - from equilibrium to chaos. *Springer Verlag, New York* **2nd Edition**.