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Two-Dimensional Modeling of a Packed-Bed Membrane Reactor for the Oxidative Coupling of Methane

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Oxidative coupling of methane (OCM) represents an opportunity for the replacement of crude oil, which still is the main source for longer hydrocarbons and almost all base chemicals, with natural gas, or biogas. OCM turns methane catalytically into mostly ethylene and ethane. Thus, several different reactor types exist, out of which the packed-bed membrane reactor (PBMR) is one of the most promising given its combination of reaction and product separation in one apparatus and also the improved temperature control because of the gradual feeding of oxygen through the membrane.
In previous simulation and optimization studies, one-dimensional models have been used to describe the conventional PBMR. However, due to radial diffusion and thermal conduction those models are not accurate enough. In this work, a two-dimensional model for the CPBMR is presented. Radial diffusion and thermal conduction in the packed-bed as well as in the reactor shell are considered while axial dispersion is neglected. In accordance with experimental studies, Knudsen's diffusivity theory is applied to describe the flux through the membrane. The model is discretized using a combination of Lagrangian and Hermite collocating polynomials on finite elements. The two-dimensional model contains second order derivatives for the radial coordinate. Hence, continuity of both the collocated variable and the first derivative across all finite elements are required in that direction. In this case, Hermite polynomials are advantageous because they allow for the afore-mentioned continuity while negating the necessity of additional equality constraints.
As an initial configuration, a length of 20 cm is assumed for the CPBMR with two separate heating/cooling segments of each 10 cm. The tube-side and shell-side diameters are set to 7 and 10 mm, respectively. Preliminary studies have shown that five radial and twelve axial finite elements are required to ensure a stable performance of all optimization studies for the given initial configuration. The resulting large-scale NLP contains more than 130,000 variables. Most fluid properties and transport parameters are implemented as functions of local temperatures and concentrations rather than average values. A brief study shows that their joint influence cannot be neglected. Using La_2O_3/CaO as a catalyst with kinetics provided by Stansch et al. (1997), an overestimation of more than 25 percentage points can be observed in the yield of C_2 hydrocarbons in a one-dimensional model in comparison to the two-dimensional case.
Optimization studies using the solver IPOPT result in operating conditions and reactor configurations with a yield in C_2 hydrocarbons of more than 40 %, which lets the two-dimensional model still appear to be more accurate than any one-dimensional case.
However, experimental studies have never shown such a performance at this level. The partial pressure of oxygen in the catalytic packed-bed of the CPBMR will always be comparatively low, usually

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below 1000 Pa, because of the diffusive flux through the membrane. Most kinetic systems for OCM are derived from micro-catalytic packed-beds and are not meant for this range. Thus, it is still questionable whether current kinetic systems are actually able to accurately describe the behavior.

1. Introduction

Replacing crude oil as the main source for longer hydrocarbons is a major challenge. As oil prices are ever increasing, alternative resources like natural or biogas become more interesting. Several process routes for turning methane into other hydrocarbons exist, among which the Oxidative Coupling of Methane (OCM) is one of the more promising alternatives.

OCM employs heterogeneous catalysis to partially oxidize and couple methane into mostly ethylene and ethane. The exact reaction mechanism depends on the chosen catalyst. Ethylene, itself, is one of the most important base chemicals used for the production of ethanol, acetaldehyde, vinyl acetate, and vinyl chloride (Atkins, 1998).

However, not the whole amount of methane is converted into C_2 hydrocarbons. Carbon oxides are also formed, and thus, necessitating a further product gas processing to separate the ethylene. The exact composition depends on a number of issues such as the catalyst type, reactor geometry, and feeding policy.

As part of the Cluster of Excellence “Unifying Concepts in Catalysis”, a mini-plant has been constructed at Berlin Institute of Technology (Technische Universität Berlin), implementing different types of reactors for the OCM process and the subsequent removal of CO_2. This contribution focuses on one particular reactor: a conventional packed-bed membrane reactor (PBMR), employing La_2O_3/CaO as catalyst. The PBMR is a cylindrical reactor consisting of an inner tube filled with a catalytic packed-bed and separated from the shell-side of the reactor by a non-selective, porous membrane. Methane and nitrogen are fed to the tube-side and oxygen and nitrogen to the shell-side of the reactor. The oxygen diffuses through the membrane allowing for comparatively low partial pressures of oxygen in the catalytic packed-bed, better temperature control and less formation of carbon oxides.

2. Problem Statement

Previously conducted work by Godini et al. (2010) used one-dimensional models for the simulation of the PBMR. However, their examination showed yields in C_2 hydrocarbons much higher than ever found experimentally or even theoretically expected. As a next step, this contribution aims at developing a comprehensive two-dimensional model for the PBMR, simulating it under isothermal, adiabatic, and heated/cooled conditions. Lastly, the stand-alone operation is optimized to assess the maximum of the possible performance of the reactor.

3. Solution Approach

The main objective for implementing a two-dimensional model is the introduction of radial diffusion and thermal conduction. Formulating a differential component balance for the tube-side of the reactor yields:

$$0 = -u_z \cdot \frac{\partial c_i}{\partial z} + D_{i,r} \cdot \left[\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial c_i}{\partial r} \right] + cr_i, \tag{1}$$

where c_i denotes the concentration of component i, $D_{i,r}$ the respective radial diffusion coefficient, u_z the superficial velocity in the reactor, and r and z radial and axial coordinates, respectively. The formation rate of each component cr_i is calculated based on Stansch et al.’s (1997) kinetics for La_2O_3/CaO. The set of differential equations is basically the same for the shell-side. Only the rates of formation are assumed to be zero. A differential energy balance for the catalytic packed-bed leads to the following differential equation for the temperature:

$$0 = -c_{tot} \cdot c_{p,tot} \cdot u_z \cdot \frac{\partial T}{\partial z} = \lambda \cdot \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} \right] + \varphi_{cat} \cdot \rho_{cat} \cdot \sum_{j=1}^{NR} rr_j \cdot (-\Delta_R H_j), \quad (2)$$

where T is the temperature, c_p the specific heat capacity, λ the effective radial thermal conductivity, and $-\Delta_R H_j$ the heat of reaction associated with reaction j. Similarly to cr_i, the rate of reaction rr_j is calculated in accordance with Stansch et al.'s (1997) kinetics. The latter term is evidently also zero for the shell-side.

The diffusive flux through the membrane is modeled using Knudsen's diffusivities and by applying Fick's law on both membrane sides. The membrane transfers heat both through thermal conduction and the diffusive flux. Both effects are modeled and the resulting heat flux coupled to both shell- and tube-side using Fourier's law. The lateral outer shell of the reactor is impenetrable to any gas components. As the OCM is strongly exothermic, a constant cooling temperature is assumed outside the outer shell and an additional heat flux is introduced for the outer shell. The total length of the CPBMR is set to 20 cm and a different cooling temperature can be defined for each segment of 10cm.

Despite the fact that almost the same partial differential equations for shell- and tube-side are implemented, thermal conductivities and diffusivities need to be calculated using different correlations. For the tube effective transport, parameters are calculated combining gas- and solid-phase. For the shell, correlations describing the gas-phase are adequate. The respective correlations published by Kee et al. (2003), Tsotsas and Schlünder (1988), Poling el al. (2001), and Bauer and Schlünder (1978) are applied. The heat transfer coefficient of the membrane is based on equations published by Specchia et al. (1980).

For solving the set of differential and algebraic equations noted above, a two-dimensional discretization is required. Given its stability properties, orthogonal collocation on finite elements is applied. Second order derivatives appear for the radial coordinate, and consequently, continuity of the first order derivative in addition to the collocated variable itself is required. To this end, Hermite H on Legendre roots and Lagrangian polynomials L on Radau roots are combined as given in Equation (3) for one single finite element:

$$f(u,v) = \sum_{i=0}^{3} \sum_{j=0}^{3} a_{i,j} \cdot L_i(u) \cdot H_j(v), \quad (3)$$

where $a_{i,j}$ are the collocation coefficients, i is the index numbering the axial collocation positions and j for the radial positions. All $a_{i,j}$ with even j refer to the actual value of the collocated variable at either outer radial edge of the finite element. All a_{ij} with an uneven j hold the value of the respective first radial derivative. For details we refer to Finlayson (1980).

The fully discretized two-dimensional model has been implemented in AMPL and solved with IPOPT. For badly scaled NLPs, it is improbable that the full-scale system can be solved without excellent starting values. Therefore, an algorithm has been developed for generating those: Initially, the system is reduced to the very first axial finite element, for which the total length is set to an arbitrarily low value, e.g. 1 µm. As close to nothing at all is going to happen within that first finite element, starting values for all variables and transport parameters can be calculated externally based on the feed streams. All radial derivatives can safely be assumed to be zero. As a next step, the first axial finite element is solved, slightly lengthened and resolved using the results of the first run. This is done until the full length required for the finite element is obtained. Afterwards, the same procedure is repeated with the second axial element based on the results of the first one.

Sensitivity studies are carried out for various purposes: finding an appropriate number of axial and radial finite elements, examining the importance of the dependence of transport parameters on local temperatures and concentrations, investigating whether it is possible to tune a one-dimensional model to mimic the 2D behavior, and for assessing the impact of each decision variable at the starting position. Afterwards, the yield in C_2 hydrocarbons is maximized. Shell and tube diameter, membrane thickness, catalyst density and volume fraction, inlet temperatures, temperature of first and second heating/cooling segment, molar fraction of oxygen in the shell-side flow and of methane in the tube-side flow are considered as decision variables. The performance of the PBMR is evaluated in all

sensitivity and optimization studies using definitions for yield and selectivity in C_2 hydrocarbons and CH_4 conversion as defined by Godini et al. (2010).

4. Results and Discussion

The following paragraphs present the results of the afore-mentioned analyses carried out on the two-dimensional model of the PBMR.

4.1 Number of Finite Elements

Using the algorithm for generating starting values, described above, the number of axial and radial finite elements is varied to find an appropriate value. The number of axial and radial finite elements is increased until after each increase the values for yield, selectivity, and methane conversion remain unchanged, i.e. only change in accordance with the set error tolerance for the solver of *1e-7*. For axial numbers of finite elements higher than ten, the yield in C_2 hydrocarbons is discovered to stay almost constant, i.e. only change in accordance with the tolerance set for the solver. Two additional, very short axial finite elements are introduced to handle fast changing profiles at the inlet and to cope with the switching point between the first and the second heating/cooling segment. At least two radial finite elements are required for the shell-side and three for the tube-side, respectively. The width of each of the finite elements in contact with the membrane should not be greater than 0.5 mm. The actual width of all other radial finite elements appears to be of no greater importance.

4.2 Reduction of Number of Variables

After determining the appropriate number of finite elements it was attempted to reduce the total number of variables of the discretized system by diffusion coefficients, thermal conductivities, and fluid parameters etc. dependent on mean temperatures and concentrations. For each individual parameter, only minor changes to methane conversion can be observed. However, as selectivity is influenced by more than half a percentage point for each and by more than 6.7 for all parameters put together, it was decided to leave all transport parameters and fluid properties dependent on local temperatures and compositions to the slight disadvantage certainly of having to handle a system with more than 130,000 variables.

4.3 Comparison of One- and Two-dimensional models

Previous studies in Godini et al. (2010) employed one-dimensional models to describe PBMRs. Table 1 compares results in yield, selectivity, and methane conversion. In addition, performance data is given for a case, in which it is tried to modify the fluxes through the membrane to tune the one-dimensional model to the two-dimensional case.

Table 1: Comparison of two- and one-dimensional models and tuning of the one-dimensional case to mimic the two-dimensional behavior.

Case	C_2 yield	C_2 selectivity	CH_4 conversion
2D	30.3 %	55.0 %	55.1 %
1D	56.1 %	77.5 %	72.3 %
1D (tuned)	30.3 %	95.4 %	31.8 %

The comparison and subsequent tuning is down for several different operating conditions, for which the results will not be given here. The picture is more or less the same for all cases. The one-dimensional system always shows a strong overestimation of the reactor's performance and reducing the fluxes through the membrane can influence the yield to mimic the two-dimensional behavior, but with a wrong distribution between selectivity and methane conversion. Obviously, it is impossible to mirror the radial influence without more complicated measures.

4.4 Tuning IPOPT

Given the size and complexity of the system describing, the PBMR it is sensible to tune the employed solver so as to reduce computation time and avoid local infeasibilities. One issue in particular will be discussed here. There are basically a variety of linear solvers which can be used for IPOPT. Table 2 compares the performance of three linear solvers for a very simple optimization case of the system

described so far, for which the optimal solution figuratively speaking lies just around the corner. MA 27 and MA 57 are both from the Harwell Subroutine Library (Hogg, 2011). MUMPS (Amestoy et al., 2011) is one of the parallel solvers available for IPOPT. Metis (Karypis and Kumar, 2006) is a package containing a number of partitioning and reordering algorithms, the latter of which probably helps to support MA 57 in order to enhance its excellent performance. The comparison is carried out in one AMD quad-core with 2.5 GHz and 8 GB of RAM.

Table 2: Performance comparison of linear solvers for a simple optimization case with a degree of freedom of one.

Linear solver	Number of iterations	CPU seconds in IPOPT	CPU seconds in NLP function evaluations
MA 27	*Gets stuck in iteration number 4, requires 5GB of RAM, no change after more than 24hours.*		
MUMPS	18	1,489.201	30.350
MA 57	19	427.899	45.163
MA 57 + Metis	19	313.900	30.258

4.5 Sensitivity of Decision Variables and Optimization Results

The results of the sensitivity analysis and the optimization will be discussed simultaneously as the final results only underline the trends found in the preceding analysis. The last optimization step shows a yield in C_2 hydrocarbons of almost 46.9 %, with a selectivity of 63.3 %, and methane conversion higher than 74.0 %. However, even a higher yield could be attained, if the bounds to the decision variables were relaxed further.

The membrane thickness increases from 50 to 65 µm. The sensitivity analyses already show that this can account for several percentage points in additional yield. The thicker membrane has one main advantage, which is the reduction of the oxygen flux into the packed-bed, and thus, avoiding carbon oxide formation and higher temperature levels. The partial pressures of oxygen are well below 500 Pa at any position of the tube-side.

While apparently causing little change at the starting point of the optimization, both the inlet temperatures and the cooling segments' temperatures are considerably lower. Consequentially, the final optimization shows an almost isothermal temperature profile with the temperature in the packed-bed staying at close to 1,050 K along both radius and axis.

With respect to the catalytic bed, a reduction of the gas phase can be observed, while the sensitivity analysis also suggests this, the effects are probably minor.

In addition, both a steady decline in the diameter of the reactor can be observed and an increase in the dilution of the shell-side's feed stream with nitrogen. Both reduce the amount of oxygen in the reactor and by minimization of the entire apparatus further allow for almost perfect temperature control. However, this movement might make sense from a thermodynamic point of view, but are economically speaking not necessarily sensible.

5. Conclusions

The results presented in this work, show that it is necessary to model the PBMR implementing the OCM two-dimensionally. A one-dimensional model cannot easily be tuned to mimic the actual behavior. While bringing about certain disadvantages with respect to finding accurate starting values, two-dimensional collocation can reliably be applied to discretize partial differential equations for cylindrical reactors. At the same time choosing the right linear solver to support IPOPT, seems to be critical so as to obtain results within a reasonable amount of time.

The stand-alone performance of the PBMR using La_2O_3/CaO as a catalyst for the oxidative coupling of methane found here is surprisingly good and cannot be backed with experimental results yet. A reason for this might be a questionable applicability of the kinetic system by Stansch et al. They derived their equations from experimental results of a fixed-bed reactor and only claim validity for partial pressures

of oxygen above 1,000 Pa. As has been mentioned above, the actual partial pressures found in the PBMR are a lot lower possibly resulting from numeric inaccuracies of the kinetic system in that range. Before continuing the theoretical work in this field, experimental studies should be carried out examining the herein found operation conditions. Nevertheless, the majority of the findings should hold true for any PBMR applying a strongly exothermic reaction.

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