DSM Science & Technology Awards 2006

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Summary Ph.D. thesis Joris Smit

Natural gas is becoming an increasingly important energy source, due to the increasing energy demands and declining oil reserves, whereas large volumes of natural gas are still widely available, especially at remote locations. In view of the existing infrastructure for liquid fuels, natural gas is most efficiently used in the transport sector by converting it to liquid fuels via the Gas-To-Liquid (GTL) process. The GTL-process consists of an air separation unit followed by a partial oxidation (POX) unit where CH_4 is converted with pure O_2 to syngas (a mixture of CO and H_2). In a third unit syngas is converted to liquid fuels via the Fischer-Tropsch reaction. Although several different syngas production technologies have been commercialised, so far the GTL-process has not found widespread application yet, mainly because of the enormous investment costs (> 1 billion US $) related to the air separation and POX units. To decrease these investment costs, two areas of possible cost reduction have been identified: improved recuperative heat exchange, which reduces the pure O_2 consumption, and an alternative air separation. To improve the recuperative heat exchange, a Reverse Flow Catalytic Membrane Reactor (RFCMR) with porous membranes is proposed in this thesis, in which very efficient heat exchange between the feed and product streams is achieved by using the reverse flow concept (*i.e.* periodic alternation of the flow direction of the gas through a fixed catalyst bed). In this novel reactor concept porous membranes (or filters) are employed to distributively feed the O_2 to the CH_4, so that hot spots and premixed feeds with the risk of the formation of an explosive mixture can be avoided. Furthermore, the porous membranes are filled with a catalyst to promote the partial oxidation reactions (*i.e.* catalytic partial oxidation, CPO). The porous membranes can be replaced by O_2 perm-selective perovskite membranes (*i.e.* a RFCMR with perovskite membranes), so that also air separation can be integrated. In this thesis these RFCMR concepts with porous or perm-selective

membranes have been developed and their feasibilities have been investigated with simulation and experimental studies.

To illustrate the importance of recuperative heat exchange for POX processes and to quantify the thermodynamic potential of both RFCMR concepts, an adiabatic thermodynamic analysis has been carried out. It was found that for POX processes with stoichiometric feeds of CH_4 and O_2 very high feed temperatures and thus very expensive high temperature heat exchangers are required to achieve high syngas yields, which is not economically feasible. When excess O_2 is used to partially preheat the feeds by combustion of part of the CH_4, lower feed temperatures suffice, but at the cost of a lower CO selectivity with respect to CO_2 and a lower H_2 selectivity with respect to H_2O. Therefore, in commercialised POX processes usually the feeds are preheated to about 700 K and O_2/CH_4 ratios of 0.6-0.7 are employed, which limits the selectivities of CO and H_2 to about 90 %. When the POX process is carried out in the RFCMR concepts, the CO and H_2 selectivities can in principle be increased up to close to 100 % and the consumption of pure O_2 can be decreased by 25-40 %, because of the improved and integrated recuperative heat exchange.

For a thorough assessment of the conceptual feasibility of the RFCMR concepts, detailed reactor models have been developed. Very similar to a conventional reverse flow reactor, the RFCMR can be described by a system of strongly coupled non-stationary, convection dominated, partial differential equations (PDE's) with strongly nonlinear source terms. Because of the steep concentration and temperature gradients prevailing in these type of reactors and the large differences in time scales of mass and heat accumulation, a numerically very efficient algorithm is required to solve the system of PDE's within an acceptable CPU time. Therefore, a numerical algorithm has been developed and programmed, which is based on a finite volume technique with implicit higher order singly diagonal implicit Runge-Kutta (SDIRK) schemes for the time integration and higher order weighted essentially non-oscillatory (WENO) schemes for the discretisation of the convection terms. Furthermore, a local grid adaptation procedure was developed that makes effective use of the smoothness indicators and interpolation polynomials of the WENO schemes and also automatic time step adaptation was incorporated. Using the simulation of a conventional reverse flow reactor, it has been shown that with the developed numerical algorithm the number of grid cells required to accurately capture the steep concentration and temperature gradients can be greatly reduced (by a factor of up to 100) and that very large time steps can be used, both of which decrease the CPU demand enormously, so that the RFCMR concepts concepts can be studied in detail.

To demonstrate the conceptual feasibility of the RFCMR concept with porous membranes, two 1-D reactor models have been developed: the Dynamic Model (DM), that takes the dynamic behaviour of the reactor fully into account and a limiting case of this model, the High Switching Frequency Model (HSFM). In the HSFM a steady state is reached, which requires much less CPU time in comparison to the DM, where it takes a long computation time to compute the cyclic steady state. Both models include a detailed description of the prevailing heat and mass transfer processes and reaction kinetics of the relevant reactions. Firstly, with HSFM simulations the RFCMR concept was further developed. It was found that a small amount of CH_4 should be combusted in the O_2 compartment just before the membrane section to establish the desired trapezoidal temperature profile and, furthermore, that a small amount of H_2O has to be added to the O_2 feed to avoid runaways in the centre of the reactor. Subsequently, DM simulations were carried out to evaluate the dynamic reactor performance in terms of syngas selectivities for different CPO catalyst particle diameters, membrane lengths, switching times and tube diameters. The simulation results showed that very high syngas selectivities (> 98 %) can be achieved for O_2/CH_4 ratios as low as 0.45, which clearly demonstrates the great potential of the RFCMR concept with porous membranes for energy efficient syngas production.

In order to evaluate the technical feasibility of the RFCMR concept with porous membranes, a demonstration unit has been constructed. Different CPO catalysts and ceramic porous membranes have been tested in a separate isothermal membrane reactor and it was shown that with a Rh/Al_2O_3 catalyst and a porous Al_2O_3 membrane very high syngas selectivities could be achieved. To determine the optimal operating conditions in the air compartment of the RFCMR (air was used instead of O_2 for safety reasons), the demonstration unit was first tested as a conventional reverse flow reactor. It was found that even small radial heat losses greatly affect the reactor behaviour, as expected, and that as a result significantly higher flow rates and CH_4 inlet fractions had to be used than would be required for an industrial scale reactor to establish the desired trapezoidal temperature profile. A reactor model has been developed that includes a detailed description of the heat loss through the insulation layer, with which the measured axial temperature profiles could be very well described. Because of the fragility and rigidness of the Al_2O_3 support tubes and porous membranes, it was very difficult to implement these in the demonstration unit. Therefore, as an alternative, a metal filter was developed, consisting of a tube in which a number of small holes were made with a laser. Subsequently, experiments were carried out in the demonstration unit at different operating conditions and it was shown that indeed very high CO and H_2 selectivities, up to 95 %, could be achieved without using any compensatory heating to counteract radial heat losses. Moreover, no hot spots were observed in the axial temperature profiles, indicating safe reactor operation. The measured axial temperature profiles could be very well described with the developed reactor model and also the agreement between the measured and predicted CO and H_2 selectivities was good. Although the maximal on-stream time of the demonstration unit was limited to about 12 hours due to cokes formation on the Al_2O_3 particles in the support tubes and because of fouling of the filter, these results clearly demonstrate the technical feasibility of the RFCMR concept with porous membranes and strongly support the results of the conceptual feasibility study.

Also for the RFCMR concept with perovskite membranes detailed reactor models have been developed and its conceptual feasibility was investigated by means of a simulation study. In order to accurately capture the influences of the local syngas composition and the temperature on the O_2 permeation rate, the O_2 permeation rate through a commercially available perovskite membrane with composition $(LaCa)(CoFe)O_{3-\delta}$ was studied experimentally in a differentially operated isothermal membrane reactor at varying operating conditions. It was found that the O_2 permeation rate is greatly enhanced in the presence of reducing gasses such as CO and H_2 on the permeate side of the membrane. Also when the temperature was increased or the membrane thickness was decreased, the O_2 permeation rate increased. From the experimental results it could be concluded that the O_2 permeation through the perovskite membrane under investigation was dominated by bulk diffusion even when a reducing atmosphere was applied at the permeate side of the membrane. The O_2 permeation rate could be well described with the Wagner equation and, when sweeping with CO or H_2, the O_2 partial pressure at the membrane surface at the permeate side of the membrane could be calculated by assuming local thermodynamic equilibrium. With the experimentally determined permeation expression, HSFM simulations were performed to determine design parameters such as the membrane length

and plateau temperature. These simulations revealed that the local heat production and consumption varies enormously along the membrane, which results in an undesired axial temperature profile and therefore also in an undesired axial O_2 permeation rate profile. This makes it very difficult to control the overall $CH_4/H_2O/O_2$ feed ratio and thus the nett heat production inside the reactor and consequently runaways were observed in the simulations. To circumvent these runaway problems, use of a porous support is proposed that acts as an additional mass transfer resistance, which is almost independent of the temperature and provides for a relatively constant O_2 permeation flux. Moreover, the porous support can be used to enhance the mechanical properties of the membrane. Provided that that a constant axial O_2 flux profile can be achieved, it has been demonstrated with DM simulations that also with the RFCMR with perovskite membranes very high syngas selectivities could be achieved, while fully integrating the air separation and recuperative heat exchange.