CFD study of CMR performance during SO_3 decomposition

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Abstract
The possibility of applying a catalytic membrane reactor (CMR) to SO_3 decomposition in a low-temperature range was theoretically evaluated with the purpose of producing CO_2-free hydrogen in an IodineeSulfur thermochemical cycle. A two-dimensional, isothermal and plug-flow model was developed for a cocurrent membrane reactor with selective permeation from the reactant stream to the permeate stream. Simulation results have revealed that CMRs can greatly reduce the reaction temperature for SO_3 decomposition from the conventional 1200-1400 K to about 900 K. We predicted that porous inorganic membranes with a high O_2 permeability and with selectivities of more than 50 for O_2/SO_3 and less than 10 for O_2/SO_2 had the potential to effectively improve SO3 conversion. CMRs were simulated to carry out SO_3 decomposition at different reaction temperatures, and pressures in feed and permeate streams. SO3 conversion at 900 K was increased to 0.93 beyond the equilibrium conversion of 0.28 due to a shift in thermodynamic equilibrium.

Keywords: Catalytic membrane reactor, SO_3 decomposition, Simulation

1- Introduction

With the simultaneous growth of the demand of global energy and of urgent concerns for reduction of greenhouse gas emissions, hydrogen has become a promising energy carrier. Currently, hydrogen is derived from nonrenewable natural gas and petroleum, but could in principle be generated from renewable resources such as biomass or water. Splitting water via a thermochemical cycle presents a viable option for largescale hydrogen production[1]. Among the large number of thermochemical cycles that can be used to split a molecule of water, the IodineeSulfur thermochemical water-splitting cycle (IS process), which was initially proposed by General Atomics, is considered an efficient, massive and CO_2-free approach [2]. The IS process primarily consists of three chemical reactions that involve the decomposition of sulfuric acid (H_2SO_4) and hydrogen iodide (HI), followed by the regeneration of these reagents using the Bunsen reaction . High temperatures equal to, or greater than, 1100 K are required to decompose H_2SO_4. The exothermic Bunsen reaction is performed at temperatures ranging from 300 to 400 K. Hydrogen is generated during the HI decomposition, using a heat source higher than 600 K.
The thermal decomposition of H_2SO_4 is actually divided into two sub-reactions:

$$H_2SO_4 \rightarrow H_2O + SO_3 \quad (573 - 873 \ K)$$
(1)

$$SO_3 \rightarrow SO_2 + 1/2O_2 \quad (1073 - 1173 \ K)$$
(2)

Both of those reactions are highly endothermic and proceed smoothly without side reactions and with a high equilibrium conversion ratio at the temperature range indicated. Fig. 2 shows the effect of temperature on computed equilibrium concentrations of components obtained from the decomposition of 1mol of pure H_2SO_4 [3]. The above two processes (1 and 2) were compared for dependence on temperature: the decomposition of H_2SO_4 to H_2O and SO_3 was predominant between 400 and 700 K while the reduction of SO_3 to SO_2 reached high conversions at temperatures higher than 1200 K. Therefore, one key challenge for the IS process is the extremely high temperatures that are required for the decomposition of SO_3 to SO_2 and O_2, which requires a substantial expenditure of energy. Recent reports have cited great potential for nuclear heat to power hydrogen production plants that utilize the IS process without producing greenhouse gas emissions [4].

A catalytic membrane reactor (CMR) is a combination of a permselective membrane and heterogeneous catalysts. CMRs have the inherent capability and advantage of combing both a reaction and a separation in a single unit. The membrane provides selective removal of products in parallel with a reversible reaction, which shifts the equilibrium towards the product side and thus results in a higher reaction conversion even at lower temperatures [5]. Because equilibrium-limited reactions usually take place at high temperatures, the membranes used for CMRs are either metal or ceramic: palladium , dense perovskite , zeolite , silica, and alumina. Considerable research effort has been devoted to the utilization of CMRs for catalytic reactions such as methane steam reforming and water gas shift reactions. Tsuru et al. [6] developed a bimodal CMR for H_2 production via the steam reforming of methane. With H_2 extraction through the membrane, methane conversion was highly enhanced from 0.44 to 0.70 at 500 C because of the equilibrium shift effect.

Therefore, in the current work as a first attitude, the SO_3 decomposition reaction in a Perovskite MR is analysed using CFD method to evaluate effects of the most significant operating parameters, namely; reaction pressure and reaction temperature for the Perovskite MR in comparison with the packed bed reactor performance. A set of simulation results is, then, provided illustrating some significant points about the Perovskite MR performance in terms of both oxygen recovery and SO_3 conversion.

2. CFD model approach

A two-dimensional, isothermal model was developed using CFD method to simulate performance of porovskite MR in comparison with convectional reactor for SO_3 decomosition .The main assumptions of this model are:

- Steady state conditions.
- Isothermal conditions.
- Infinite O_2 perm-selectivity of porovskite membrane with respect to other gases.

- Reaction occurs only at the catalyst surface, so there is no mass transfer resistance between the bulk gas and the catalyst surface.
- Flux equations of permeating components for both kinds of membranes were derived from single gas permeation test at different temperatures.
- Physical properties, such as gas density, are constant with temperature.
- The film transport resistance supposed at the interface of gas/membrane was considered negligible.
- Pseudo-homogenous condition in reaction zone.

The last assumption means that the catalyst surface and bulk fluid have the same conditions and, as a result, the behavior of both phases can be considered by the same variables.

2.1. Governing equations

Briefly, the model is mathematically expressed by the governing equations consisting of continuity equation (Eq. (3)), momentum balance (Eq. (4)) and species transport-reaction equation (Eq. (5)):

$$\nabla(\rho_f.\varepsilon.u) = S_i \tag{3}$$

$$\nabla(\rho_f.u.u.\varepsilon) = -\nabla p - \beta u + \nabla \tau + \rho_f g \tag{4}$$

$$\nabla(\rho_f.u_i.\varepsilon) = \nabla(\rho_f D_{i,e}\nabla m_i) + (1-\varepsilon)\rho M_i \sum_j v_{ij}R_j + S_i \tag{5}$$

In the equations above, β is the friction coefficient given by the following equation (we assume $\varepsilon = 0.6$ and $dp = 5mm$):

$$\beta = \frac{150\mu_f(1-\varepsilon)^2}{\varepsilon.d_p^2} + \frac{1.75(1-\varepsilon)\rho_f}{\varepsilon^3 d_p}|u| \tag{6}$$

m_i is the mass fraction of species i, R_j is the reaction rate with a corresponding stoichiometric coefficient v_{ij}, ε is the void fraction of the packed bed and S_i is the source/sink term. For the reaction zone, which is packed with catalyst pellets, the model includes the reaction terms (R_j denotes the rate of a reaction j), the sink term (S_i) that accounts for O_2 removal by the membrane, and the friction term ($\beta.u$) to account for pressure losses along the packed bed. There is no catalyst in the permeate zones ($\varepsilon = 1$) and, therefore, there is no reaction there ($R_j = 0$).

2.2. Reactions and rate experssions:

- SO_3 decomposition reaction[7]

$$SO_3 \rightarrow SO_2 + 1/2O_2 \tag{7}$$

$$r_d = \frac{\left(k_s K_{SO_3} p_{SO_3}\left(1 - \frac{p_{SO_2} p_{O_2}^{0.5}}{p_{SO_3}}\frac{1}{K_e}\right)\right)}{\left(1 + K_{SO_3} p_{SO_3} + K_{SO_2} p_{SO_2} + K_{O_2}^{0.5} p_{O_2}^{0.5}\right)^2} \tag{8}$$

$$k_s = 1.38 \times 10^{10} e^{\frac{-1.54 \times 10^5}{RT}} \tag{9}$$

$$K_{SO_3} = 5.32 \times 10^8 e^{\frac{-2.3 \times 10^5}{RT}} \tag{10}$$

$$K_{SO_2} = 2.65 \times 10^{22} e^{\frac{-5.1 \times 10^5}{RT}} \tag{11}$$

$$K_{O_2} = 3.75 \times 10^{34} e^{\frac{-8.1 \times 10^5}{RT}} \tag{12}$$

- Membrane Flux equation for O_2 separation [8]

$$J_{O_2} = A|e^{-E_a/RT_m}\frac{T_m}{b_m}\ln\left(\frac{p_{O_2}^{shell}}{p_{O_2}^{tube}}\right)\text{mol}/(m^2 \cdot s) \tag{13}$$

2.3. Solving stratgey

Numerical simulations were performed using the commercial CFD package COMSOL Multiphysics 5.4 The finite-element method was used to solve the governing equations in the two-dimensional CFD model for present work. Moreover, pressure-velocity correction was done using the SIMPLE algorithm. Dependences of fluid density, viscosity, diffusivity, thermal conductivity and heat capacity on temperature, pressure and composition were accounted for using standard definitions built-in in the computation software. A small fraction of O_2 at the reaction zone entrance was used to prevent numerical problems that shoot from the appearance of oxygen partial pressure in the denominator in kinetics equations. Furthermore, the solution was considered achieved when the residuals converged to values less than the magnitude of 10^{-4} and all the variable values were not changed with iteration.

2.4. Model validation

The accuracy of our CFD model was verified versus experimental data measured in meng et al. work [7]. Fig. 1 shows the SO_3 conversion and hydrogen recovery versus reaction pressure for the porovskite MR during SO_3 decomposition reaction. The operating conditions for the porovskite MR model are (at 1 bar, T=800 K). It can be seen that the simulated values are in a good agreement with the reported modeling values. A comparison between CFD and modeling results reveals that the error ranges between 2 and 5%.
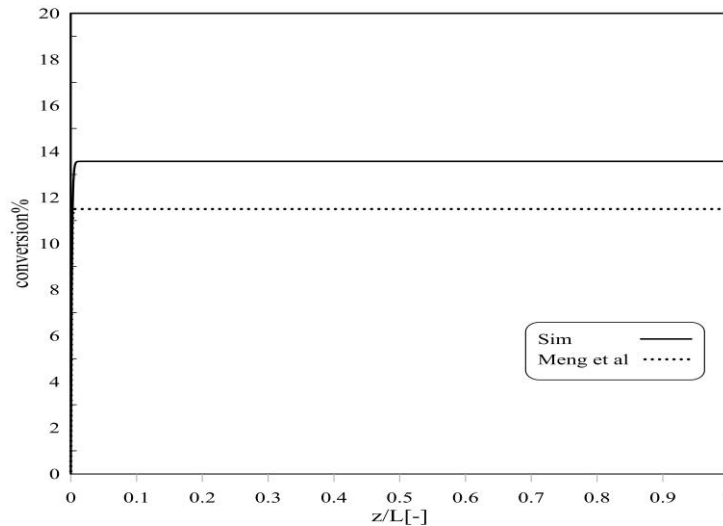
Fig.1. SO₃ conversion versus dimentionless length

3.Results and discussion

A parallel CFD study has been carried out for comparing the effect of most important operating conditions on the performances in terms of SO_3 conversion and oxygen recovery of the MRs equipped with provskite membrane during MSR reaction. In particular, effects of reaction pressure and sweep gas ratio (SGR) were investigated.
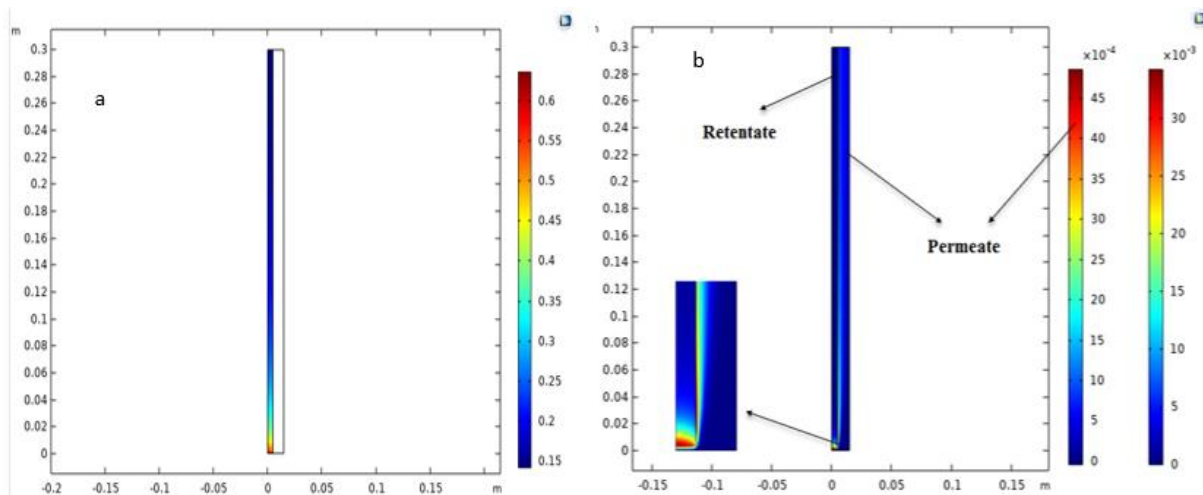

Fig.2. Concentration contours achieved by CFD simulation during SO₃ decomposition in psovskit MR; (a): SO₃ concentration distribution (mol/m³), (b): O₂ concentration distribution (mol/m³).

3.1. Evaluation of temperature and pressure effect on reaction

The influence of reaction pressure on the both MRs performance in terms of SO_3 conversion and oxygen recovery was investigated. The results are shown in figure 3 and according to the below figures which both temperature and pressure in MR cause to SO_3 conversion and O_2 recovery.By increasing the retentate side pressure, the driving force of oxygen diffusion from the membrane is enhanced: this increases the oxygen recovery. By removing the oxygen from

the reaction zone, on the basis of Le Chatelier's principle, the forward reaction of SO_3 decomposition is thermodynamically favored, and this leads to higher conversions of SO_3. On the basis of reaction rate (Eq. (8)) and oxygen permeation flux (Eq. (13)), which have an Arrhenius equation type dependency on the temperature, by increasing the temperature both SO3 conversion and rate of oxygen permeation are increased. On the other hand, due to the increasing the oxygen recovery at higher temperatures, the difference between SO_3 conversion in MR and TR increases too.

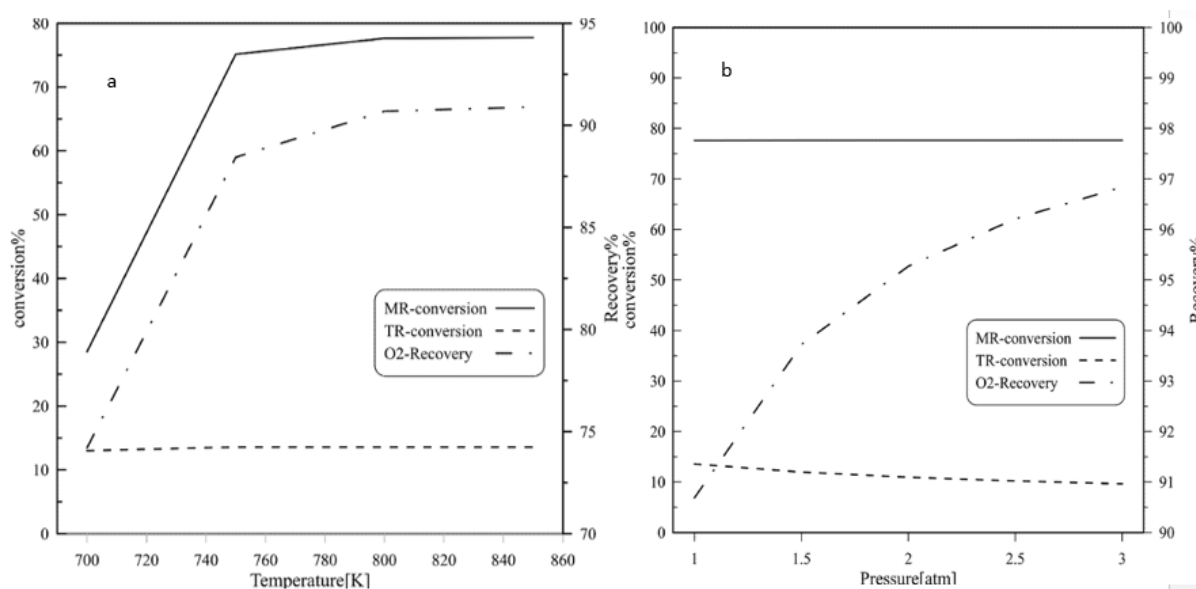**Fig.3. SO_3 conversion and O_2 recovery in both MR and TR versus temperature (a)and pressure (b)**

4. Conclusion

In this work, performance of provskit MR were compared for oxygen production from CFD point of view. To this purpose, a 2D-axisymmetric, isothermal model was developed using CFD method for evaluation mentioned MRs performance during SO_3 decomposition reaction. The simulation predictions showed very good agreement with modeling over a large range of operating conditions in terms of SO_3 decomposition and total oxygen recovery. The proposed CFD model is able to provide detailed description of component fraction, velocity and pressure distribution in the both MR modules, thus allowing further analysis of driving force variation.

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