Numerical Simulations to Evaluate Different Approaches for Scaling up of Packed Bed Membrane Reactor for HI Decomposition

Nitesh Goswami, Soumitra Kar, R.C. Bindal and P.K. Tewari
Desalination Division

and

K.K. Singh
Chemical Engineering Division

Abstract

Evaluation of different approaches to scale up PBMR (Packed Bed Membrane Reactor) for HI decomposition has been carried out using numerical simulations. Numerical simulations involve coupled solution of momentum, energy and species transport equations. The results suggest that, to produce hydrogen at large scale, it is better to use several small diameter reactors in parallel than using a single large diameter reactor or a single longer reactor.

Introduction

Extensive research is being carried out in BARC by different groups of researchers for addressing various critical issues associated with production of hydrogen by thermochemical splitting of water by IS process. Efforts are being made for the development of membrane-based processes applicable to HI processing stream. In this regard, Desalination Division, BARC is associated with the development of silica-based membrane reactor for enhancement of equilibrium decomposition of HI. An attempt has been made to develop silica membrane [1] on alumina support with graded porosity using sol-gel processing. A prototype membrane reactor has also been developed in-house.

IS thermochemical process is one of the promising processes of hydrogen production amongst all the alternatives available keeping in view of the predicted thermo-chemical efficiency and possibility to couple it to a high temperature nuclear reactor [2]. The IS process consists of following reactions:

\[ \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4 \quad (\text{the Bunsen reaction}) \]  

(1)

\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 0.5\text{O}_2 \]  

(2)

\[ 2\text{HI} \rightarrow \text{H}_2 + \text{I}_2 \]  

(3)

The third reaction is HI decomposition reaction in which \( \text{H}_2 \) is produced. Activated charcoal is one of the potential catalysts for this reaction. \( \text{H}_2 \) is the product, \( \text{I}_2 \) is recycled into the Bunsen reaction. In the overall reaction, \( \text{H}_2\text{O} \) is decomposed into \( \text{H}_2 \) and \( \text{O}_2 \). The equilibrium conversion of decomposition of HI is very low which increases the costs and efforts involved in production of \( \text{H}_2 \) from this cycle. Kar et al. [3] cited that the low decomposition ratio leads to reduction in the thermal efficiency of the cycle. One of the methods to enhance the decomposition of HI could be based on hydrogen permselective membrane reactor. A membrane reactor is a single unit integrating both reaction and membrane-based separation. It can also be termed as membrane-based reactive separation. Several studies on computational fluid dynamics (CFD) modeling of the membrane reactors have been reported in literature. CFD modeling of ammonia cracking inside a catalytic membrane reactor has been reported by Carlo et al. [4]. Marin et al. [5] reported a 2D membrane reactor model involving momentum, mass and energy transport. The model was validated with experimental data of the methane steam reforming reaction. Smith et al. [6] analyzed the performance of a membrane reactor...
for low temperature water gas shift reaction using CFD simulations. While the CFD modeling of membrane reactors for other reactions do provide useful information, the results and conclusion obtained for one reaction may not be applicable directly for other reactions due to change in kinetics, heat effects and physical properties. The objective of this paper is to evaluate different approaches for scaling up a PBMR for HI decomposition using the numerical simulations.

**Computational Approach**

A commercial package COMSOL Multiphysics has been used to carry out the numerical simulations which involve solution of momentum, energy and species transport equations. Brinkman equation and Maxwell-Stefan equation have been used for momentum and mass transport, respectively. For energy transport, both conductive and convective heat transfer have been considered. Variation of properties like viscosity, density, heat capacity etc. with temperature and pressure are taken into account in the model by using the suitable equations.

For HI decomposition which is an endothermic reaction, a Langmuir-Hinshelwood type rate equation, proposed by Oosawa et al [7] for the catalytic decomposition of HI using an active carbon catalyst, is used for carrying out the simulations. The relevant expressions are given by Eqs. (4) – (8)

\[
\begin{align*}
    r_{HI} &= \frac{-k p x}{1 + K_{12} P x_{12}} \\
    R_{HI} &= \sqrt{\frac{x_{HI} x_{12}}{1 + K_{12} P x_{12}}} \\
    k &= 1.58 \times 10^{-11} \exp \left( \frac{-E_{a1}}{RT} \right) \\
    K_{12} &= 5.086 \times 10^{-11} \exp \left( -\frac{E_{a2}}{RT} \right)
\end{align*}
\]

Where, \( p \) is pressure, \( x \) is mole fraction, \( r_{HI} \) is the rate of reaction (mol/m^3.s), \( K_{12} \) is coefficient of adsorption of iodine, \( E_{a1} \) is 34.31x10^3 J/mol and \( E_{a2} \) is -86.66x10^3 J/mol [8]. \( \Phi_e \) is the equilibrium conversion (0.21 at 700K). The equilibrium constant, \( K_p \), for the decomposition of HI is obtained by the free energy values given in the JANAF [9] using the following equation:

\[
K_p = \exp \left( -\frac{\Delta G}{RT} \right)
\]

Where, \( \Delta G \) is 11.5 kJ/mol at 700 K.

Grid independence test is done to decide the grid density to be used for carrying out the simulations. The computational approach adopted in this study has been validated using the experimental data reported for steam reforming of methanol in a packed bed tubular reactor [10]. Complete details of the computational approach used in numerical simulations are reported elsewhere [11].

**Results**

Three approaches to scale up from a small-scale reactor are possible. In the first approach several identical small-scale reactors can be placed in a parallel flow arrangement. In the second approach, the small-scale reactor can be made longer to provide the same residence time as in the small-scale reactor. In the third approach, the diameter of the small-scale reactor can be increased to provide the same residence time as in the small scale reactor. All the three approaches were evaluated using two-dimensional numerical simulations. Other parameters which affect the performance of the reactor e.g. reactor wall temperature, feed temperature, feed composition, outlet pressure, porosity of the bed, diameter of the particles and membrane permeability were kept same. The values are given in Table 1.

A small-scale PBMR of 1.5 m length and 0.1 m diameter having feed velocity 0.01 m/s was considered as the base case. Scale up by a factor of 2 was considered. The first simulation was for the small-scale reactor itself. In the second simulation, a PBMR (longer reactor) with length and feed velocity twice of that of the small-scale reactor was considered. In
the third simulation, a PBMR (wider reactor) having width twice of that of the small-scale PBMR but having the same feed velocity and length as the small-scale PBMR was considered. Fig. 1 shows the variation of mole fraction of H₂ inside the reactors as predicted from numerical simulations. Fig. 2 shows the temperature field inside the reactors as obtained from numerical simulation. Table 2 compiles important data obtained from the numerical simulations.

**Discussion**

The hydrogen mole fraction profiles in Fig. 1 show that very less hydrogen is present in the central zone near the inlet. This is because the feed in the central zone takes some distance to feel the effect of wall temperature and reach the reaction temperature. This distance increases with increase in feed velocity and reactor width, as seen in Fig. 2. This causes the average temperature in the wider PBMR to be lower than in the small-scale PBMR which causes the average reaction rate and conversion to be lower in the wider reactor than in the small-scale reactor. Thus, two small-scale reactors in parallel is a better scale up approach than having a single wider reactor. Despite longer preheating length due to high feed velocity, the average rate of reaction in the longer PBMR is more than that in the small-scale PBMR. The pressure drop is very high in the longer PBMR. Since the outlet pressure is maintained constant, a higher pressure drop causes average pressure inside the longer PBMR to be higher. The higher pressure causes average hydrogen permeation flux and average reaction rate to be higher in the longer PBMR than in the small-scale reactor. Despite being wider, pressure drop in the wider PBMR is more than that in the small-scale PBMR. This is due to higher viscosity of the reaction mixture owing to lower mean temperature in the wider PBMR. Since

<table>
<thead>
<tr>
<th>Table 1: Operating parameters and properties of the packed bed and membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall temperature (T_w)</td>
</tr>
<tr>
<td>Feed temperature (T_f)</td>
</tr>
<tr>
<td>Outlet pressure (p_0)</td>
</tr>
<tr>
<td>Membrane permeability (P_e)</td>
</tr>
<tr>
<td>Packed bed porosity (ε)</td>
</tr>
<tr>
<td>Mole fractions in feed</td>
</tr>
<tr>
<td>Particle diameter</td>
</tr>
</tbody>
</table>

![Fig. 1: Mole fraction profile of H₂ inside the PBMRs](image-url)
the outlet pressure is same for all the reactors, average pressure in the wider PBMR is more than the average pressure in the small-scale PBMR. This causes the average permeation flux to be slightly higher in the wider PBMR than in the small-scale PBMR despite of the conversion being more in the small-scale PBMR. Though the average reaction rate in the longer PBMR is more than that in the small-scale PBMR, conversion in the longer PBMR is lower than that in the small-scale PBMR. Since pressure drop is more in the longer PBMR, for the same outlet pressure and same feed velocity, the density of the feed mixture and hence the mass flux at the inlet of the longer PBMR is more than the same for the small-scale reactor. The increased reaction rate in the longer PBMR is not able to offset the increased mass flux causing the conversion to be smaller in the longer PBMR than the small-scale PBMR despite of higher average reaction rate in the longer PBMR. The pressure drop inside the small-scale PBMR is lower and the conversion is slightly higher than that in the longer PBMR. Hence, using parallel small-scale PBMRs reactors is a better scale-up alternative than using a longer PBMR. Due to very small conversion, using a wider PBMR is not an appropriate option for scaling up.

**Conclusion**

Different approaches for scale up of PBMR for HI decomposition have been studied by the numerical simulations. A small-scale PBMR reactor gives 83.4% conversion. The conversion obtained in the longer PBMR having twice the feed velocity of the small-scale PBMR is 82%. The wider PBMR having

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Average temperature (K)</th>
<th>Average reaction rate (mol/m³.s)</th>
<th>Pressure drop (N/m²)</th>
<th>Average H₂ permeation flux (mol/m².s)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small-scale PBMR</td>
<td>689.14</td>
<td>0.116</td>
<td>2717</td>
<td>7.64×10⁻⁵</td>
<td>0.834</td>
</tr>
<tr>
<td>Longer PBMR</td>
<td>688.69</td>
<td>0.123</td>
<td>1888</td>
<td>7.85×10⁻⁵</td>
<td>0.819</td>
</tr>
<tr>
<td>Wider PBMR</td>
<td>668.96</td>
<td>0.086</td>
<td>4519</td>
<td>7.68×10⁻⁵</td>
<td>0.608</td>
</tr>
</tbody>
</table>

**Table 2: Important data resulting from numerical simulations**

**Fig. 2:** Temperature field inside the PBMRs (scale in Kelvin)
width twice that of the small-scale PBMR gives only 61% conversion. The conversion obtained in the longer PBMR is almost same as that obtained in the small-scale PBMR but pressure drop is much higher. Hence, it is concluded that to produce hydrogen at large scale, it is better to use several small-scale PBMRs in parallel than using a single longer PBMR or a single large diameter PBMR.

Acknowledgement

Authors are thankful to Head, ChED, BARC for allowing access to computational resources.

References


