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CFD based optimization of Water Gas Shift Membrane Reactor

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Abstract: In the Hydrogen based economy, distributed power generation systems using fuel cell technology require modularity. This modularity in power generation can be achieved by process intensification of the equipments involved. The water gas shift reaction is an integral part of hydrocarbon based Hydrogen generation and the reaction is kinetically limited and hence occupies the largest volume. Process intensification of the water gas shift reactor and the hydrogen separator leads to a membrane reactor. Computational Fluid Dynamics was used in this study to analyze a Palladium based water gas shift membrane reactor and the optimum operating conditions for the same were identified and reported.
Keywords: membrane reactor, CFD, time factor, water gas shift reaction.

1. Introduction

Fuel Cell technologies are driving the development of portable power systems like remote community power generators and onboard power generators for transportation sector. In these hydrocarbon based power generators, the process flowsheet involves reforming of fuel (production of syngas) followed by water gas shift reactor, gas separation and fuel cells. Since portable generators have to be modular, efforts are on to miniaturize these operations. Micro reactors for fuel reforming are being developed. The water gas shift reaction which performs the dual role of reducing the carbon mono oxide content and enriching the hydrogen content in the synthesis gas is kinetically limited and hence occupies the maximum volume [1]. Hence it is imperative that this process component be modified to suit modularity. One process intensification step that helps in this route is the membrane reactor technology whereby both the reaction and separation can be achieved in a single process vessel. Membrane reactors have the advantages of reduced size of vessel, increased conversion of CO (due to continuous removal of product the equilibrium shifts to the right) and effective separation of H_2 in a single vessel.

Water gas shift reaction is a moderately exothermic reversible reaction expressed by

$CO + H_2O \leftrightarrow CO_2 + H_2$

$\Delta H^0_{298} = -41.09$ kJ/mol …… (1)

The reaction is thermodynamically favoured at low temperatures and kinetically favoured at high temperatures. Since there is no change in the volume from reactants to products, the reaction is not affected by pressure. The reaction is traditionally carried out in a series of two packed beds namely a high temperature

catalyst bed followed by a low temperature catalyst bed. The high temperature catalyst is made of ferro chrome and operates at 673K whereas the low temperature catalyst operating at 473K is a combination of Cu, Al_2O_3 and Cr_2O_3/ZnO. Considering the operating temperatures in the portable power generators, the low temperature catalysts can be used. Recent research is towards the development of noble metal catalysts for the water gas shift reaction. Even though hydrogen can be permeated by both organic and inorganic membranes, inorganic membranes are suitable owing to their mechanical strength and temperature tolerance. Various studies carried out show that ceramic porous membranes, metallic dense membranes and ceramic/metal supported thin metallic membranes can be used for this application. The most studied membrane for water gas shift reaction is Palladium alloys with Silver and Copper due to their higher selectivity and permeability to Hydrogen.

Several studies have proved the effectiveness of membrane reactors for water gas shift reaction. Kikuchi [2] have reported complete conversion using a membrane reactor. Uemiya [3] used a Pd membrane (20 μm) supported on porous glass in concentric tubular configuration and achieved CO conversion more than the equilibrium conversion. Basile [4, 5] using Pd and $Pd_{77} - Ag_{23}$ supported on alumina analyzed the effect of temperature, H_2O/CO, feed flow rate, pressure and time factor on the performance of water gas shift reaction in a membrane reactor. Near to 100% CO conversion have been reported with sweep gas, higher pressure, temperature and time factor. The optimum temperature for the reaction was found to be 600K. Comparisons of Pd (70μm) membrane reactor and Pd/Ag (50μm) membrane reactor by Basile [6] have shown the Pd/Ag membrane reactor giving close to 100% conversion. Criscuoli [7] compared the performance of Pd, Pd/Ag and mesoporous reactors of similar volume on three different gas feed mixtures and found the Pd/Ag membrane reactor reporting up to 100% conversion at higher time factors and 595K. The high temperature operation of water gas shift reaction was carried out by Iyoha [8, 9] in multi tubular membrane reactor with Pd and Pd/Cu membranes in the absence of catalysts. The Pd membrane reactor achieved a conversion of 99.7% while the Pd/Cu membrane reactor showed 66 – 68% conversion. But the Hydrogen recovery from both the reactors stood at 85 – 90%. Basile [10] analyzed the possibility of using Pd membrane reactor for producing hydrogen capable to be fed to fuel cells. Brunetti [11] has carried out experiments on Pd/Ag membrane reactor using a mixture of gases and found that with the same reaction volume CO conversion achieved in the membrane reactor was 3 to 5 times higher than that could be achieved in a traditional reactor. Recently Barbieri [12] have proposed a combination of traditional reactor followed by membrane reactor as a single reactor to carry out the water gas shift reaction so as to prevent back permeation. With this configuration they could achieve 93% conversion without sweep gas using Pd /Ag membrane (60μm). The influence of co current mode and counter current mode of operation of the membrane reactor was carried out using simulation by Basile [13]. They found both modes of operation giving same conversion with increased H_2 recovery in the counter current operation. Chiappetta [14, 15] found the increase in lumen pressure of the reactor having a positive effect on the hydrogen recovery. By analyzing the safety aspects in the membrane reactor, they found that using high pressures can also reduce the hot spots in the reactor. Mendes [16] has made a review of the water gas shift reaction in membrane reactors. Sjardin [17] has identified temperature, pressure, steam to CO ratio, time factor and sweep flowrate as the key operating parameters in a membrane reactor.

Computational fluid Dynamics (CFD) is increasingly used in the process industry to design and optimize reactors and other process vessels. It is an effective tool to analyze fluid flow and also the associated reactions in various systems. It is based on the following governing equations of fluid flow namely;

(i) Continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho \vec{\upsilon}) = S_m \qquad \ldots\ldots (2)$$

(ii) Momentum equation

$$\frac{\partial(\rho \vec{\upsilon})}{\partial t} + \nabla.(\rho \vec{\upsilon}\vec{\upsilon}) \quad -\nabla P + \nabla.(\bar{\bar{\tau}}) + \rho \vec{g} + \vec{F}$$

$\ldots\ldots\ldots(3)$

(iii) Energy equation

$$\frac{\partial(\rho E)}{\partial t} + \nabla.(\vec{\upsilon}(\rho E + P)) \quad \nabla.(K_{eff} \nabla T - \sum_j h_j \vec{J}_j + (\bar{\bar{\tau}}_{eff}.\vec{\upsilon})) + S_h$$

$\ldots\ldots\ldots(4)$

(iv) Species transport equation

$$\frac{\partial(\rho Y_i)}{\partial t} + \nabla.(\rho \vec{\upsilon} Y_i) \quad -\nabla.\vec{J}_i + R_i + S_i \qquad \ldots\ldots..(5)$$

2. Geometry and Boundary Conditions

The experimental results of [7] are taken as the basis for the simulation as this is a study carried out with different compositions of feed gases and operating conditions. The geometry of the membrane reactor used in the simulation is made of two concentric tubes namely the lumen and shell. The lumen is made of the membrane material and is packed with catalyst and this region acts as the reacting side. The membrane zone has an inner diameter of 8 mm and length of 150 mm representing a total reactor volume of 7.5 cm^3. The shell has an inner diameter of 40 mm with provision for sweep gas inlet and the overall length of the reactor is 280mm. The catalyst particles were assumed to be spherical particles having a constant diameter of 1mm each. Further, porosity of the bed of 0.457 has been imposed in the simulations and the above values have been arrived based on the physical characteristics provided by Criscuoli [7]. The characteristics of the catalyst used by Criscuoli [7], represent Topsoe make (LK-821-2) with the following properties; Composition $CuO–ZnO–Al_2O_3$, Density 2400 (kgm^{-3}), Specific Heat 687 ($Jkg^{-1}K^{-1}$), Thermal Conductivity 1.163 ($Wm^{-1}K^{-1}$), Porosity 0.457, Permeability $2.158x10^{-9}$ m^2, Inertial Resistance 19912 (m^{-1}) and Surface area/volume 3256 (m^2m^{-3}).

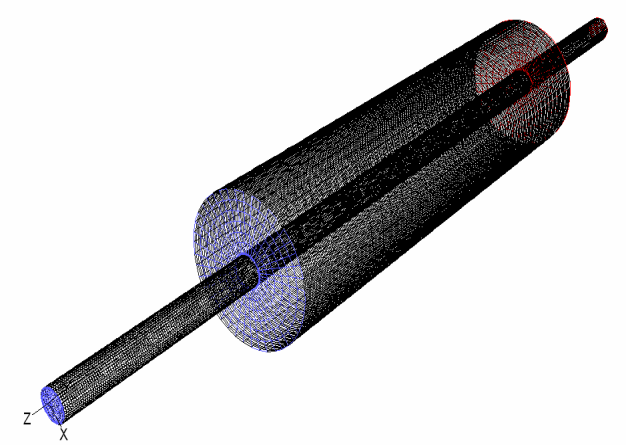

Fig 1 Grid for membrane reactor

The 3D geometry of the reactor described above was generated using the pre-processor GAMBIT 2.3 and solved using FLUENT 6.3, a commercial CFD code based on finite volume methodology using Cartesian co-ordinate system. The geometry was discretized using unstructured grids, with number of nodes varying as 198828, 284130, 418232 and 753559. Boundary layers were generated on either side of the membrane with the first row having a thickness of 0.1mm. One cell thick zones were segregated on either side of the membrane to apply the permeation of hydrogen. Custom designed User Defined Functions (UDF) has been developed to impose the volumetric reaction, source terms and momentum terms into the solver. Simulations using these grid sizes were compared for flow parameters and CO Conversion and the grid size corresponding to 284130 nodes provided sufficiently accurate results without further improvement with increase in number of cells and hence is used for the simulation (Fig 1). The velocity profile and pressure drop computed by the simulation were similar with that values computed manually.

The simulations have been carried out assuming that the flow represents a three dimensional, steady state, incompressible, laminar flow with isothermal conditions. Further, the gas has been assumed to obey ideal gas equation. The incompressible flow has been imposed in the simulations as the maximum velocity of the gas inside the packed bed reactor represent Mach number < 0.3, indicating density variations are negligible. The binary diffusion coefficients used in computations have been computed using the Fullers Equation [18] and fitted as a second order polynomial equation. The reaction is modeled using pseudo homogeneous reaction approach since the porosity of the bed was constant owing to smaller regular particle size and the extent of reaction was considered uniform all along the length of the reactor. Thus volumetric reaction rate were sufficient to model the reaction kinetics. The solutions have been obtained using segregated solver approach with second order upwind scheme for discretization. The SIMPLE (Semi Implicit Pressure Linked Equation) algorithm was used for the pressure velocity coupling with pressure term discretized using the PRESTO (Pressure Staggering Option) scheme, whose predictions were found to be better for porous bed. The convergence criterion was fixed as 1E-05 for momentum equations and 1E-07 for all other equations. The CFD simulations were carried out for three gas mixtures of different compositions designated as mix1, mix2, and mix3. These mixtures represent the compositions expected in gasification and reformed synthesis gases. Mix 1 and Mix 2 are typical compositions found in gasification. Their compositions on dry basis are

Mix 1 CO (32 %), CO_2 (12 %), H_2 (4 %) and N_2 (52 %)
Mix 2 CO (12.27 %), CO_2 (11.49 %), H_2 (75%) and CH_4 (1.24 %)
Mix 3 CO (27%) and H_2 (73%)

The simulations solved the flow equations of continuity, momentum, species and energy equation. The simulations were carried out in three stages.

Initially, the case was set up and simulated without Hydrogen permeation and reaction occurring in the reactor. Once the residuals stabilized, the user defined functions corresponding to permeation through the membrane are activated and the simulations are continued till the residuals again stabilized. Finally the reaction mechanisms are invoked to complete the simulation.

3. Results and Discussion

The important operational parameters that affect the performance of membrane reactors are Temperature, Pressure, time factor, sweep flow rate (N_2) and steam to CO ratio. Since experimental studies by Criscuoli et al [7] has found 595 K as the optimum operating temperature, all the simulations were carried out at the temperature. Kinetic screening studies on packed bed reactor by the authors using five different macro kinetic models taken from [19] have found the Langmuir Hinshelwood model and Temkin model better predicting the reaction and hence have been employed in this study. The study and comparison with the experimental results further showed that the Temkin model could better predict the performance of the water gas shift membrane reactor in relation to the Langmuir Hinshelwood Model. In a membrane reactor, the permeation is directly proportional to the partial pressure difference of Hydrogen across the membrane. To achieve higher driving force for permeation, there are two operational possibilities. One is to increase the operational pressure of the feed gas and the other is to involve an inert gas as sweep gas in the annular region. To study these effects, simulations were carried out with sweep gas and without sweep gas to analyze the influence of increasing lumen pressure on the performance of the reactor. The sweep flow provided the maximum conversion possible for Mix 1 and 3 and hence increasing pressure had no significant effect on them. But Mix 2 showed an increase in conversion and H_2 recovery with increasing pressure and the effect became less significant after 2.5 atm. Without sweep gas, the influence of lumen pressure is significant in both Mix 2 and Mix 3 which are rich in H_2. To identify the effect of steam to CO ratio on a membrane reactor, simulations were carried out by keeping the temperature, pressure and sweep gas flow constant and varying the feed gas mixture as per the various steam to CO ratios. The simulations indicate an optimum steam to CO ratio of 2 – 2.5 for all the three mixtures.

Even though the operating pressure and sweep gas utilization are dependent on the nature of the process and the prevailing upstream conditions, based on the simulation of these parameters the following optimum conditions are put forth. The optimum conditions are a trade off between the CO conversion and the H_2 recovery. For Mix 1, the time factor can be 4140 g min/CO mol, steam to CO ratio be 2.5, trans-membrane pressure difference be 1atm with Nitrogen sweep flow of 436 ml/min. Mix 3 too can be operated at the conditions as same as Mix 1. For Mix 2 which is thermodynamically less active, fixing the time factor is very difficult as the conversion keeps improving with increasing time factor. But since the requirement is for modular applications, the smallest time factor is preferred. This mixture can be operated with steam to CO ratio of 2.5, nitrogen sweep of 436 ml/min and a trans-membrane pressure differential of 1.5 atm. The simulated results obtained are provided in Figures 2-4.

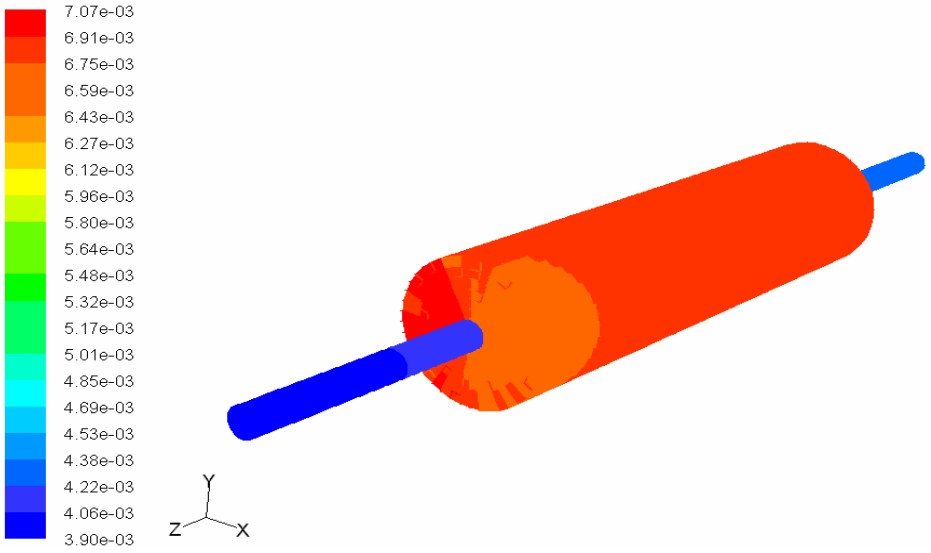

Fig 2 H_2 contour for time factor 4140 g min/CO mol, 595 K, sweep flow rate of 436 ml/min,

lumen pressure of 2 atm, shell pressure of 1 atm and steam to CO ratio of 2.5

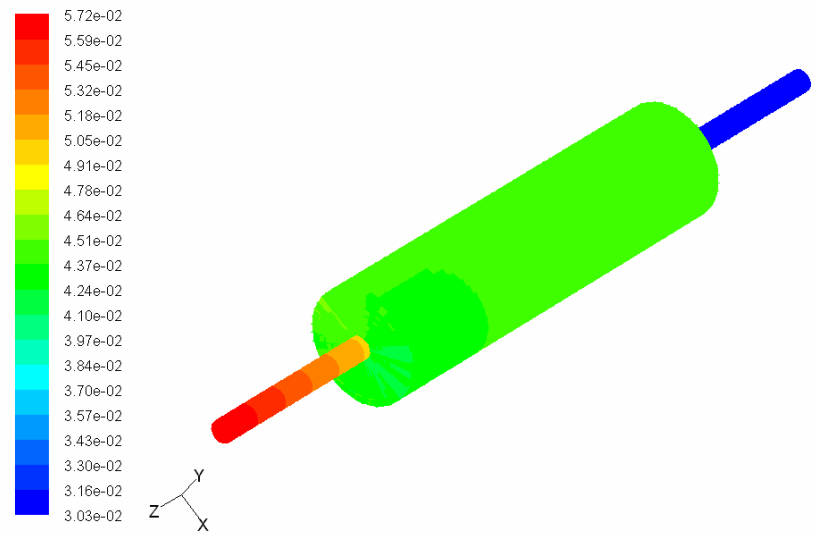

Fig 3 H_2 contour for time factor 4140 g min/CO mol, 595 K, sweep flow rate of 436 ml/min, lumen pressure of 2.5 atm, shell pressure of 1 atm and steam to CO ratio of 2.5

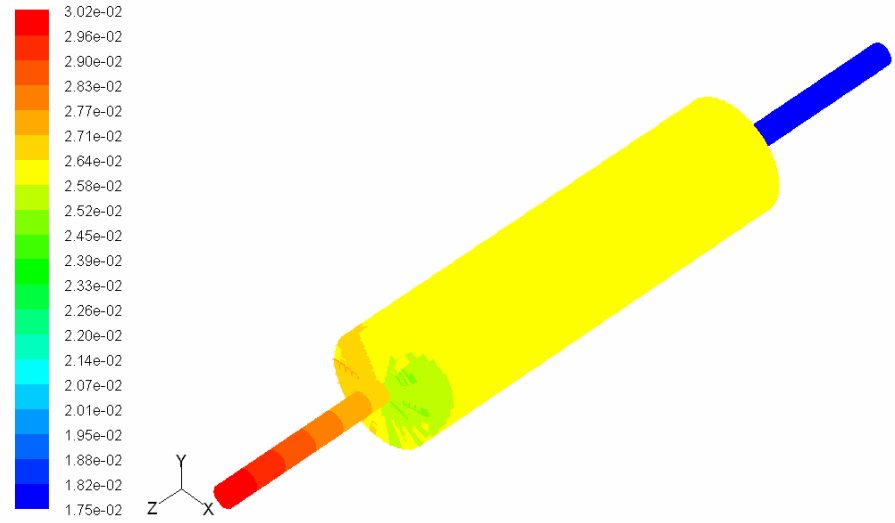

Fig 4 H_2 contour for time factor 4140 g min/CO mol, 595 K, sweep flow rate of 436 ml/min, lumen pressure of 2 atm, shell pressure of 1 atm and steam to CO ratio of 2.5

4. Conclusion

The water gas shift converter in a modular power generation system can be reduced in size by the process intensification of the reactor and H_2 separator stages into a single unit. The membrane reactor thus used poses engineering challenges in its design and scaleup as both reaction step and permeation step has to be incorporated in the same reactor. Computational Fluid Dynamics offers an option of virtual walk through the reactor. The detailed study of the three gas mixtures with various operating parameters for the water gas shift reaction in a Palladium membrane reactor has shown the optimum operating conditions for the reaction.

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