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Process Intensification Aspects for Steam Methane Reforming: An Overview

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Steam methane reforming (SMR) is the most widely used process in industry for the production of hydrogen, which is considered as the future generation energy carrier. Having been perceived as an important source of H_2, there are abundant incentives for design and development of SMR processes mainly through the consideration of process intensification and multiscale modeling; two areas which are considered as the main focus of the future generation chemical engineering to meet the global energy challenges. This article presents a comprehensive overview of the process integration aspects for SMR, especially the potential for multiscale modeling in this area. The intensification for SMR is achieved by coupling with adsorption and membrane separation technologies, etc., and using the concept of multifunctional reactors and catalysts to overcome the mass transfer, heat transfer, and thermodynamic limitations. In this article, the focus of existing and future research on these emerging areas has been drawn. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 408–422, 2009
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Introduction

Hydrogen is considered as the next generation energy carrier that can offer a nonpolluting, inexhaustible, efficient, and potentially cost effective energy source for the future. The most important aspect of hydrogen as a fuel is that it reduces greenhouse gas effect: a problem that is now more pronounced with the recent concern about global warming.[1] Hydrogen economy involves producing hydrogen from different energy sources (natural gas, coal, etc.), transportation and storage in an efficient manner, and effective coupling of production/storage strategy with the end use applications. Among these, the most important aspect which has major potential for energy intensification is the hydrogen production. This demands that the existing methods for H_2 production should be reviewed extensively for energy efficiency, environmental concerns, and economics.

As far as the existing H_2 production technologies are concerned, the main pathways are thermal, electrochemical, or biological (Figure 1). Among these methods, the thermal method, specifically steam methane reforming (SMR), in which methane reacts with steam to produce a mixture of hydrogen, carbon dioxide, and carbon monoxide, is the most widely used. Today, almost all the hydrogen is produced by SMR in oil refineries. The majority of this is used for upgrading fuels and commodities. SMR accounts for over 48% of H_2 production globally[2] and the main feedstock is the natural gas. However, the efficiency of SMR is 65–75% for the best of the commercial productions[3] and any efforts to increase the efficiency would have significant impact on the H_2 economy.

Process intensification (PI) is an effective strategy to achieve increased energy efficiency. PI aims at reducing the mass and heat transfer resistances while overcoming thermodynamic limitations through integrated design and operation.

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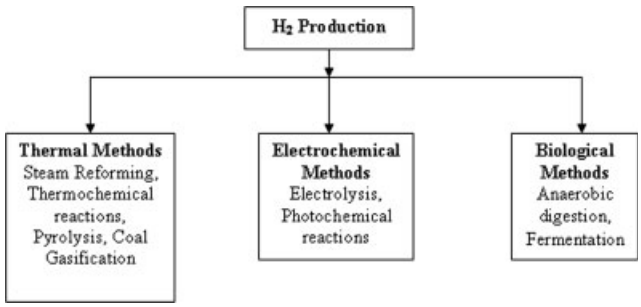

Figure 1. Methods for H_2 production.

Recent advances in fuel cell technologies as a compact energy source coupled with the progress in separation technologies and catalysis have triggered efforts in intensified SMR design. This involves integration of various processes occurring in the reformer as well as coupling with pre- and postprocesses such as purification, carbon sequestration, combined heat, and power generation (Figure 2). The traditional process of steam reforming in catalytic tubes surrounded by huge furnaces has now evolved through modification in three major areas to address issues of diffusional limitations,[4,5] thermodynamic limitations,[6] and catalyst deactivation due to coke formation,[7] etc. This involves changing from fixed bed to fluidized bed operations, change of heat supply from external firing to direct heating, and in-situ separation of one of the products to drive the reaction beyond its thermodynamic equilibrium.[8] This is achieved by combining SMR with adsorption,[9] membrane separation,[10] etc., to overcome thermodynamic limitations, mass transfer enhancement through multifunctional particle design,[11] improved heat transfer through coupled catalytic reactors[12] and plasma technology,[13] and novel catalyst design to achieve desirable kinetics. All these configurations involve coupling one or more functionalities in the reactor design and give an additional degree of freedom[14–17] in the optimal design of such systems. One of the important advancement is achieving reaction enhancement to enable a lower operational temperature, which in turn may resolve the problems associated with catalyst fouling as well as help in realization of a compact domestic H_2 source.

Intensification of SMR, thus, involves consideration of mechanisms at microscale occurring on catalysts, multifunctional particles to macroscale design, and operation of intensified processes, e.g., adsorptive, membrane catalytic reactors. Therefore, multiscale modeling framework integrating the phenomena at these scales can offer suitable computational framework for optimal manipulation and control. The future technology for SMR will see compact, easy to use, and highly integrated SMRs for power generation, specifically, for fuel cell applications. In this article, we have reviewed the existing scenarios for intensifying SMR and have highlighted future trends. The insights into process intensification will also require focus into detailed kinetic modeling for SMR within an integrated framework especially considering the multiscale issues. The second section in this article deals with the advances in the kinetic modeling. First the conventional modeling aspects are briefly highlighted followed by discussion on the multiscale modeling framework and its role in the design of intensified multifunctional catalysts. The third section describes the novel concepts in intensified SMR reactor design using membrane reactors. The fourth section highlights the use of adsorptive reactors for selective removal of CO_2. Recent developments in compact reactors to overcome heat/mass transfer limitations are discussed in the fifth section. The sixth section presents conclusions and future research directions in these areas.

Modeling of SMR

SMR involves following sets of reactions:

$$\begin{aligned} &CH_4 + H_2O \leftrightarrow CO + 3H_2 && \Delta H_{298} = 206\ \text{kJ/mol} && \text{(a)} \\ &CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 && \Delta H_{298} = 164.9\ \text{kJ/mol} && \text{(b)} \\ &CO + H_2O \leftrightarrow CO_2 + H_2 && \Delta H_{298} = -41\ \text{kJ/mol} && \text{(c)} \end{aligned} \quad (1)$$

Reactions (a) and (b) are strongly endothermic whereas reaction (c) is mildly exothermic. The stochiometric balance indicates that the first two reactions (a) and (b) are favored by decrease in pressure whereas the reaction (c) remains unaffected as per Le Chatelier's principle. Selective removal of CO_2 from the reactor is another option that will favor higher conversion of CH_4. In industry, these reactions are carried out as a two-step process. The first step is reforming [reactions (a) and (b)] and is carried out at 750–800°C to produce synthesis gas (mixture of CO and H_2). The second step is the water gas shift (WGS) reaction [reaction (c)], which involves catalytic reaction of CO with steam to form H_2 and CO_2. This step essentially involves a high-temperature shift (HTS) at 350°C followed by a low-temperature shift (LTS) at 190–210°C. Thus, the two important areas to achieve energy efficiency are, clearly, separation of CO_2 to increase the equilibrium conversion (mass transfer and thermodynamic issues) and efficient heat integration (heat transfer issues).

The kinetic modeling aspects play a crucial role in process integration specially to establish the compatibility with the coupled processes. A detailed understanding of the SMR kinetics helps in addressing the potential of process intensification and to assess the benefits achieved thereof. This section will review the kinetic modeling efforts in SMR. The research in modeling SMR has been toward the development of reaction kinetic mechanisms and evaluation of kinetic parameters. Initial approaches were approximate and involved assumptions regarding the rate limiting steps[18–20] under the experimental conditions studied. Kinetic parameters such as

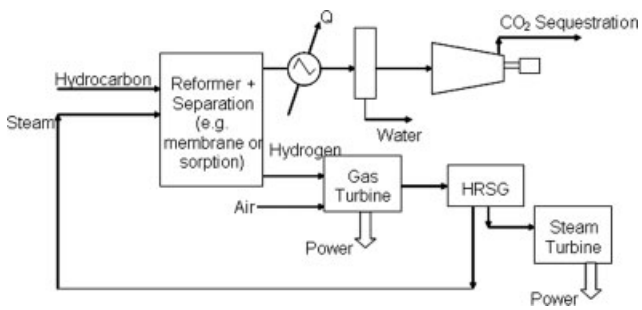

Figure 2. SMR and the postprocesses.

the rate constants and order of reaction were obtained from the experimental results. The lack of fundamental molecular analysis behind these approaches made them unsuitable for the use in the range outside the experimental range used for tuning the parameters. However, the increase in computational power has now enabled detailed molecular phenomena to be incorporated into the modeling framework to give more meaningful picture. Figure 3 highlights the evolution of kinetic modeling approaches. The molecular dynamic theories are now being used to predict the parameters associated with the reaction mechanisms.[21,22] The important reaction mechanisms are identified to calculate overall kinetics. This information, however, cannot be used as such at the macrolevel, i.e., the scale of industrial operation. It is, therefore, important to transfer this information to the higher scale in an efficient manner. This requires identification of various scales (length and time) of importance, development of models for these different scales and coupling the information across these scales in an efficient manner. This is the main objective of multiscale modeling. Such approach can be used to identify the rate limiting parameters at the molecular level, establish their correlation with parameters at macrolevel and then control the macroscale parameters by manipulation at the microscale. This approach is capable of addressing issues ranging from computational catalyst design to overall reactor design and optimization. In the field of SMR, although there are some efforts in the area of microkinetic modeling, development of a detailed framework for its integration with mesoscale and macroscale is still at the primitive stage. In this section, we first briefly summarize the initial efforts in kinetic modeling followed by the recent trends in microkinetic modeling and potential for multiscale modeling.

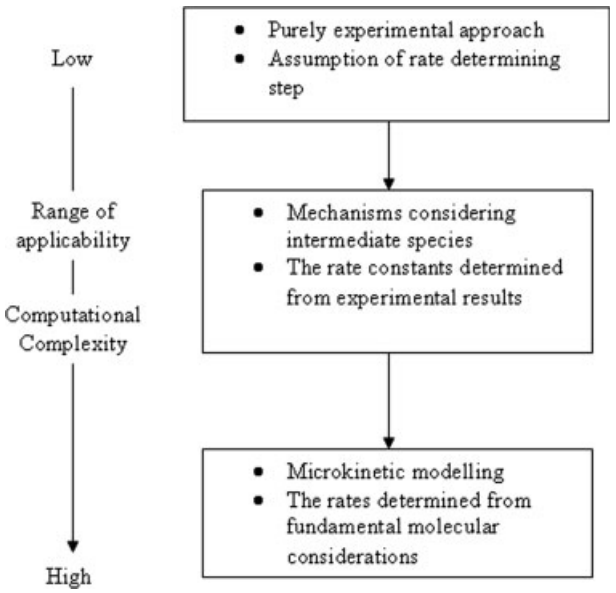

Figure 3. Evolution of reaction kinetic approaches for SMR.

Initial efforts in kinetic modeling[23] involved SMR using porous Ni catalyst and Ni foil covering a large temperature (260–1000°C) and pressure (1–50 atm) range. In most of these studies, the rate of reaction was established to be dependent on partial pressure of methane, water, and products. First detailed efforts involved experimental investigations into the existence of short lived intermediate species and its incorporation into kinetic modeling by Schnell[24] who also established dependency of reaction rates on the structure of catalysts and suggested that the composition of catalysts plays a major role on the kinetics of SMR. Various alloys have been tested as catalysts and the activities of intermediate species were found to be important parameters affecting the performance of catalysts.[25,26] The main drawback of all the initial approaches is that these involved empirically based power law kinetics with the assumptions regarding the proposed reaction mechanism. The evaluation of empirical parameters was done from the experimental data. Such approaches result in model inadequacies that lead to many drawbacks as well as discrepancies. PI involves interaction of SMR with the other associated processes and such approach may cause diverse unstable effects on the integrated framework [not illustrated in the following sections]. One of the most interesting contradictions in SMR kinetics was the prediction of positive[4] as well as negative effective reaction orders[14–17] with respect to steam. All these drawbacks were, however, overcome by the model of Xu and Froment.[27,28] These workers focussed on detailed reaction kinetic mechanism to model intrinsic kinetics of SMR reactions on $Ni/MgAl_2O_4$-spinel catalyst. Their proposed reaction scheme consisted of 21 sets of rate equations. The rate equations were expressed in terms of the concentration of the adsorbed species. The concentrations of the relevant species were then eliminated by means of Langmuir equilibrium relation, and the balance on the active sites including the vacant sites as well as those covered by adsorbed species. This resulted in a rate expression in terms of gas phase partial pressures and adsorption coefficients. Model discrimination and parameter estimation using the experimental data on steam reforming resulted in rejecting five sets out of the 21 sets of rate equations. Thermodynamic consistency was also taken into account. The intrinsic parameters so derived were used in the simulation of the commercial reactors. Diffusional limitations were incorporated through the evaluation of tortuosity factor, effective diffusivities, and the effectiveness factor. These parameters were used in the steady state simulation of the industrial steam reformer with satisfactory results.[28] The rate expression developed by Xu and Froment[27] is more generic and can explain a number of contradictions in the previous works described earlier.[4,20,29] This generic kinetic framework is being widely used in modeling industrial reformers till today. Later, Elnashaie et al.[30] carried out parametric study of this model over a wide range of parameters and showed a nonmonotonic dependence of the reaction rate on the steam partial pressure. This gave rise to an interesting optimization problem with feed partial pressure of steam as the decision variable. However, steam to feed ratio is kept at 4–6 in industrial operations to avoid coking problem.

The approaches stated above still have drawbacks because they involved some assumptions or empiricism at one stage or the other. A fundamental approach using molecular considerations is the most preferred one, but is very time consuming. However, the increase in the computational power has now prompted detailed investigations into the microki-

netic modeling of SMR kinetics. This will be the focus of future kinetic modeling efforts in almost all the areas in chemical engineering. These approaches involve establishing the reaction mechanism and evaluation of the kinetic parameters by using detailed theoretical approaches or using semi-theoretical and experimental approaches. Microkinetic models utilize parameters, such as sticking coefficients, surface bond energies, pre-exponential factors, and activation energies for surface reactions, surface bonding geometries, active site densities, and ensemble sizes, etc., that are measured independently or calculated theoretically using tools such as theories of chemical bonding.[21,22] Such approaches are generic and allow incorporation of fundamental microscopic events in the development of the kinetic framework. Such modeling tools are very important from the catalyst design point of view. The microkinetic modeling approaches have, thus, rendered detailed and more meaningful analysis of the SMR.

Aparicio[31] proposed microkinetic modeling of SMR over Ni catalyst by carrying out transient isotopic studies and the mechanism involving various surface events occurring on the Ni catalyst. It was observed that there was no single rate-determining step in methane reforming with either steam or CO_2 for a wide range of operation of SMR, and there was no simple rate expression valid over this entire range. Under some conditions, the availability of surface oxygen may play a key role in determining the rate. Such detailed analysis helps in effective manipulation of the operating conditions to obtain optimal behavior in a standalone or an integrated framework. Other such approaches[21,22] obtained kinetic parameters by estimating the activation energies and the pre-exponential factors on the basis of absolute rate theories such as transition state theory, bond order conversion Morse potential (BOC-MP), etc. Chen et al.[22] also used this approach for catalyst design. It was observed that lower binding energy of C—M bond results in a lower conversion, but at the same time much lower potential for carbon formation. Using the microkinetic model, a preferred optimal binding energy window of C—M of 160–169 kcal/mol and H—M of 64–67 kcal/mol was identified and used as a guideline for the selection of promoters and dopands for Ni catalysts. This study proves the potential of microkinetic modeling for catalyst design.

Although there were lots of research efforts toward kinetic model development for SMR, many studies with different degree of complexities for WGS reactions alone have also been developed. Various reaction mechanisms (e.g., redox, formate, associative, and the carbonate mechanisms) for kinetic analysis of WGS reaction are characterized based on the formation of different intermediate species in the SMR.[32] The more complex reaction mechanisms involve combination of one or more of these kinds of mechanisms with some additional new elementary reaction steps. The most comprehensive and practically useful among them are the reaction mechanisms proposed by Mhadeshwar and Vlachos[33] and Callaghan.[32] The former involved a reduced kinetic model using principle component analysis and posteriori analysis, whereas the latter involved a reaction route graph theory approach to arrive at a reduced reaction rate. An important emphasis of these proposed mechanisms was to extract the maximum possible significant information from the detailed molecular framework and apply it with a more computationally realizable modeling framework for practical implementation.

The application of the parameters derived from microkinetic models to the higher level mean-field models involves assumptions regarding the homogeneity of catalytic surface. However, there can be significant nonuniformities in catalytic surfaces and these can significantly affect the overall performance of the catalyst and the SMR. To incorporate these nonuniformities, we need to use models at the length scale of catalyst surface. These mesoscale models need to be accounted in between the micro (microkinetic approach) and the macro (reactor scale) frameworks thus giving rise to a multiscale framework (See Figure 4). Much needs to be done in this area, and this is going to be the focus of research in

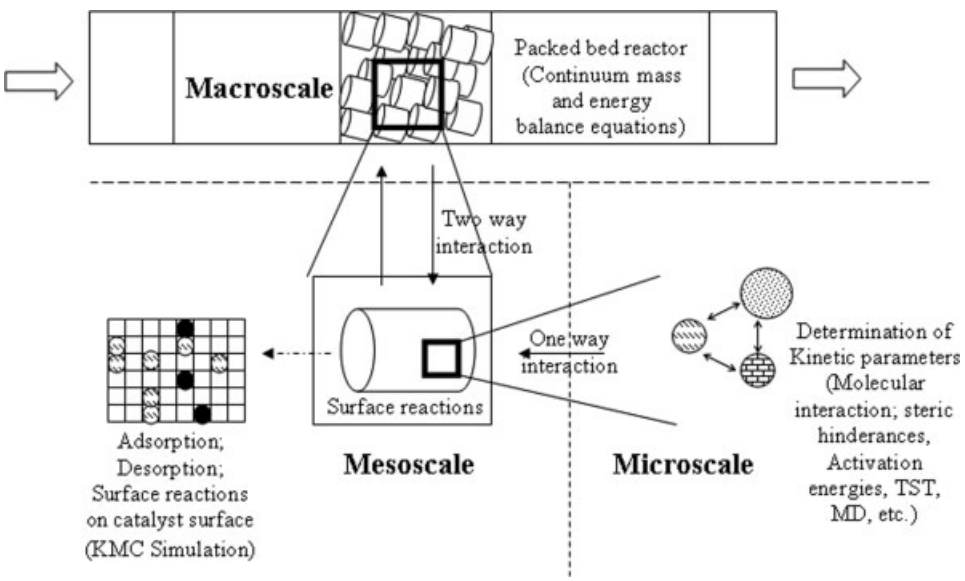

Figure 4. Multiscale modeling approach.

the future not only for SMR but for almost all the existing chemical processes. The most suitable modeling framework to incorporate the events on the catalyst surface is the Kinetic Monte Carlo (KMC) simulations.[34] These involve evaluation of surface configuration using a probabilistic framework. The probabilities of various events are derived based on the kinetic reaction parameters derived from microkinetic approach and the mole fraction of the gaseous species in the bulk (macro) phase. The information flow from the micro to meso (KMC) is one way. There is no feedback from KMC to the microkinetic modeling approach. However, the coupling between the KMC and the macroscale is bidirectional through dependence of KMC on the gas phase mole fraction and dependence of macroscale models on the surface coverages obtained using KMC simulation. The length and time scale at which KMC simulations are performed are much smaller than the macroscale and KMC needs to be accelerated using time and length coarse graining techniques.[34]

The temporal coarse graining for KMC involves concepts such as partial equilibrium (PE) for very fast processes and evaluating slower processes stochastically.[35] The problem with this approach, however, is its inefficiency if the separation of time scales is moderate. Resat et al.[36] have proposed a weighted probability KMC approach in which several events of fast reactions are simultaneously implemented while a slow reaction takes place. This is based on the fact that during slow reactions the transition probabilities of fast reactions and the concentration of species do not vary significantly. However, the problem with this approach is that the weighted probabilities tend to amplify noise associated with KMC. A more efficient approach is the net event KMC approach[37] where reversible reactions are treated as one event (the net rate is taken as the difference between the forward and backward reactions). The better aspect of this strategy is that this is self adjusted and behaves as regular KMC when there is no separation of scales. The temporal acceleration is achieved as the equilibrium is attained. However, this strategy causes noise reduction and it is not possible to study the role of various fluctuations in the KMC framework. An improved version of the weighted probability KMC approach is the τ-leap method originally proposed by Gillispie[38] and its adaptations.[39,40] These approaches are considered very promising for temporal acceleration. The basic idea in the τ-leap method is the selection of the time increment τ which is larger than the time increment associated with the microscopic event. During this time, multiple faster events are executed. The frequency of occurrence of the events is sampled from Poisson distribution.

As far as spatial acceleration of KMC is concerned, the basic idea is the coarse graining of the Hamiltonian using wavelets.[41] In this scheme, the coarse cells containing several microscopic cells are considered. The mean field approaches are assumed in the coarse cells. The interaction potential and transition probabilities are coarse grained using wavelets. The most important aspect for successful implementation of this strategy is to ensure that both the microscopic as well as macroscopic scales are correctly captured. Coarse grained KMC simulations usually tend to show large errors at interfaces and boundaries where large gradients exist. This requires adaptive coarse graining techniques[42] for reducing errors. Both these spatial and temporal acceleration methods can be implemented in a combined framework to accrue the advantages of both.[43] Integration of the τ-leap method along with the coarse grained KMC method has been considered as the best combination to achieve acceleration in both time and space.[34] As far as application of these strategies for SMR is concerned, the challenge is in developing detailed reaction mechanisms and estimating the rate parameters using molecular framework. The combined space and time acceleration strategies can then be further used to achieve useful insights into the macroscopic framework of industrial interest.

The role of multiscale modeling is specifically important in an integrated framework as it can help in assessing various degrees of freedom in the integrated framework in a more meaningful way for better process performance. Various issues in terms of the compatibility of various integrated processes, limiting conditions, and their enhancement through manipulation at micro–meso–macro scale can be effectively addressed. An important application of SMR is in fuel cells as a compact source of H_2. This demands compact reformers using efficient catalysts and processing conditions. The multiscale modeling is an effective approach that can tackle this challenge in a meaningful way. This approach can identify key parameters for a better SMR design through better catalysts design and inclusion of multifunctionality in the reactor/catalyst design, in conjunction with the objective of delivering a stable H_2 supply from fuel cells under changing load conditions. This is going to be a major driving force for future research in design of SMRs.

It must be emphasized that the advantage of multiscale modeling approach compared with the conventional empirical approaches is not very significant in terms of better prediction of conversions and/or yield (as the existing empirical models can be tuned online to arrive at equally good model predictions), but in its applicability (because of detailed microscopic aspects) for better molecular insights of the process. Such insights are helpful for exploiting additional degrees of freedom at molecular level such as through catalyst design. As far as existing empirical models are concerned, these are still important from industrial point of view as they can be used for online optimization and control by tuning the model parameters using online measurements. The multiscale modeling framework will not be suitable for such online applications considering the large computational time involved. However, insights from multiscale modeling are always important to develop improved models for online applications.

Intensified SMR Design Using Membranes

Membranes are finding increasing applications in the global market as an important separation/filtration alternative and the market is exponentially growing with new polymeric membranes being produced. Heterogeneous catalytic gas-phase reactions with membrane modules usually involve membrane materials such as Group VIII metals, polymeric, ceramic, or zeolite membranes for selective separation of one or more components. Membranes act as permselective membranes or form a part of catalytically active surface. The combined effect of reaction and membrane separation can overcome thermodynamic limitations and can get almost 100% methane conversion at lower temperatures.[44] Thus,

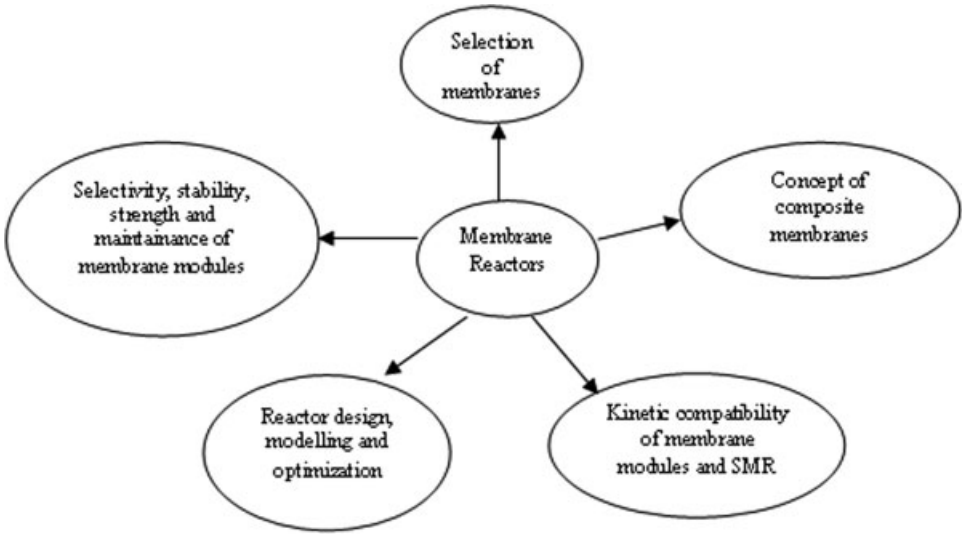

Figure 5. Various aspects of membrane reactors for SMR.

SMR membrane modules are considered very significant from fuel cell application point of view.

The issues related to membrane reactors involve choice of a suitable membrane for a given product quality and throughput required. For a given membrane material, it is important to assess the effect of feed quality and operating condition on the stability and robustness of membrane. Other important factors that must be considered are the mass transport characteristics of the membrane material, purity of the hydrogen required, and the pressure at which it is obtained, factors affecting membrane fouling, etc. The improvement in the performance of membrane reactors, specifically for industrial applications, needs to integrate these aspects within the SMR reactor framework both from design and operation point of view. Figure 5 highlights these important aspects of membrane SMRs. In an integrated framework, the bottomline is the compatibility of the separation of either CO_2 or H_2 by the membrane with the rate of production.

The membranes which are most widely used for H_2 separation are Pd based as this is a highly H_2 selective permeation material.[45] But these membranes are very expensive. Industrial application requires less expensive and high permeance membranes with complete selectivity and good stability. This can be achieved by using a composite membrane with a thin Pd-based layer supported on a porous substrate. Porous glass, alumina, and other metals are often employed as substrates and are proved to be good.[46–48] However, there are concerns like mechanical strength and different thermal expansion coefficients that create obstacles. Recently, Tong et al.[49] used Pd/CeO_2/MPSS membrane that overcomes these drawbacks and achieves 97% methane conversion at 500°C. Dense ceramic (perovskites) and mixed ceramic–metal membranes are of potential use[50] for selective separation of H_2 at high temperatures. However, detailed information on structural performance is required for their efficient use and is being investigated.[51] Modified perovskite membranes[52–55] have been investigated by many researchers along with Ni based catalysts. Specifically $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$[52–54] and $SrCo_{0.5}FeOx$[53,55] membranes have shown high throughput rates that are close to commercialization targets.[56] However, these membranes are not preferred commercially due to issues related to decomposition of perovskite into two phases and the difficulties in achieving methane conversion and CO selectivities higher than 95%.[57] High-temperature porous membranes, e.g., silica, silicalites, and zeolite,[58–60] have the advantage of lower price and higher permeance than Pd-based membranes. Among these, microporous silica shows the highest H_2 selectivities with the H_2/N_2 selectivities exceeding 10,000 for some cases.[61–63] Polymeric memebranes that selectively permeate H_2 over CO_2 are also important candidate for SMR. For a wide range of polymers the H_2/CO_2 selectivity vary between 0.5 and 2.5.[64,65] For alumina supported styrene-divinylbenzene membranes even higher permeabilities (i.e., 500–4000) have been reported for H_2. However, for all these membranes, achieving high H_2 permeability with high H_2/CO_2 selectivity is still an important challenge and needs to be explored.

Important parameters affecting performance of membrane reactors are operating pressure, temperature, membrane thickness, membrane reactor length, etc. Among these the membrane thickness is the most important construction parameter.[66] Significant efforts in the development of membrane reactors considering these aspects for SMR were undertaken by Adris et al.[67,68] These authors have carried out both experimental and numerical investigations on the use of hydrogen selective membranes to overcome the thermodynamic equilibrium barrier in bubbling fluidized bed membrane steam reformer (BFBMSR). An improved circulating fast fluidized bed membrane reformer (CFFBMR)[69] further overcomes the limitations of the BFBMSR specifically in terms of flexibility, fluid dynamic limitations, and ability for continuous catalyst regeneration. Figure 6 gives the schematic of CFFMBR. The coupling of the endothermic steam reforming and exothermic oxidative reforming in CFFBMR gives the advantages of producing H_2 with high yield and energy savings. H_2 productivity of CFFBMR is about 112 times better than that in a bubbling fluidized bed membrane reactor. The sensitivity analysis and optimization of CFFBMR can help

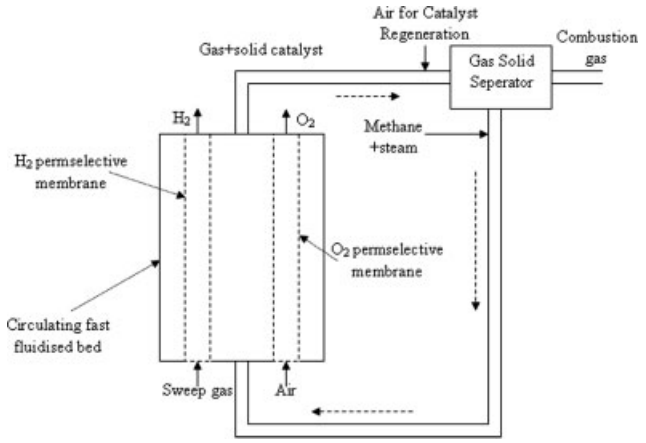

Figure 6. A schematic of circulating fast fluidized bed membrane reformer.[69]

further improve the H_2 productivity. The other important issues of concern are catalyst deactivation and control configuration for these kinds of reactor configurations.

Significant developments have been reported in various reactor configurations under both kinetic[70,71] and equilibrium conditions.[72,73] These studies were aimed at determining the effect of various parameters such as reaction temperature and pressure, steam to methane ratio, sweep gas velocity, and the operating mode (cocurrent or counter current) on the overall performance. However, these studies did not discuss the important issues such as evaluation of membrane area and energy requirements that ultimately affect the fixed and operating costs of the plant specifically in an integrated framework with other processes. Recently, Bottino et al.[74] proposed a model for nonadiabatic industrial SMR under equilibrium conditions to study the effect of operating parameters on these two important aspects. Their investigations revealed that temperature profile plays a significant role in process economy and development of thin and permeable membranes is a key issue for improving the performance of large industrial plants.

Optimization of membrane SMR reactors requires robust models for better evaluation. There are various one dimensional approaches in the modeling of membrane reactors which are only good for laboratory scale units.[75] However, for industrial scale units, there are radial temperature and composition gradients, and these affect the calculation of tube wall and membrane temperatures, the driving force for H_2 flux, etc. Falco et al.[75] proposed a two-dimensional model and observed that integration of membrane in reformer improves the performance through the promotion of reaction rate by high temperature near the hot wall and by H_2 removal in the low-temperature central zone. Such detailed investigations give a meaningful picture to optimize the process performance specifically for a multiobjective optimization framework.

It is important that simulation studies for membrane reactors for SMR should be carried out in conjunction with the entire power process to achieve overall productivity. The input to and feedback from various upstream and downstream processes may result in a more robust and meaningful picture. Other important issue is the study related to kinetic compatibility of the hydrogen production and its removal using a membrane. Such studies help in estimating membrane area using the permeability coefficient and hydrogen produced. In membrane reactors, sweeping gas is generally used to gain permeation driving force and there is always a limiting conversion in a cocurrent or counter-current sweep gas flow rate. Hara et al.[76] have pointed out that the limiting conversion is always largest in the counter-current mode and the complete conversion can be obtained at 500°C or more. At lower temperatures, the complete conversion cannot be obtained even using a long reactor.

Membrane reactor technology is quite advanced and widely studied in literature and the recent emphasis is on the development of better membranes, more efficient reactor configurations, and better modeling approaches for analysis and optimization. The generic microkinetic modeling approach for SMR can be used along with the detailed transport equations for membranes to formulate more robust models. These models can further be used to optimize the process performance, specifically with respect to the two most important factors: the area of the membrane and the energy consumption, in an integrated framework.

Sorption Enhanced Steam Methane Reforming

There are substantial advances in the use of membrane for steam reforming. However, there are many practical issues, such as pore blockage causing low permeation rates, expensive membrane materials, limited thermal and mechanical stability, the complex design of reactors, etc., that hinder the usefulness of the membranes separation strategies. This has lead to the development of adsorption enhanced process configurations. Process of adsorption offers some distinct advantages in terms of the tolerance of materials to high-temperature and pressure, wider range of availability of adsorbents for desired separations, and sorption kinetics of the same order of magnitude as the reaction kinetics. However, in contrast to membrane separation where the desired component can be distinctively separated (either in pure form or with a diluent in a sweep gas mode), the adsorption phenomena, by its inherent nature, requires an additional step for regeneration of the adsorbent. Commonly used regeneration strategies include temperature[77] (TSA) and pressure swing[9,78] (PSA) operations. Recently, Reynolds et al.[79] developed a rigorous process simulator for high temperature PSA cycle using K-promoted hydrotalcite as CO_2 adsorbent at 525 K. Effect of operating parameters, such as purge-to-feed ratio and cycle step time, on the process performance was studied in terms of CO_2 recovery and enrichment. At 100% recovery, enrichment of 2.6 was obtained and at 87% recovery enrichment of 3.9 was obtained. These results show the potential of high-temperature PSA cycle for carbon capture. As far as TSA is concerned, recently, Lee et al.[80] proposed a strategy that combines SMR with TSA directly producing fuel cell grade hydrogen. A K_2CO_3 promoted hydrotalcite was used as CO_2 chemisorbent. This is periodically regenerated at 590°C by purge steam. Simulation results indicated the feasibility of developing a very compact H_2 production unit with very less requirement for regeneration steam. As far as TSA and PSA

technologies for regeneration are considered, the former does not use rotating machinery (vacuum pump) or part of the product for pressurization and hence ensures more recovery of hydrogen. In the future, optimal design of PSA or TSA cycles in conjunction with SMR holds the key for efficient SMR operation and its relative usefulness over other similar intensification strategies.

First application for adsorptive reactors[81] dates back to 1868 and a patent[82] in 1933 for a continuous process producing H_2 at the pressure of 1–50 atm and temperature 300–550°C. Limestone was used as adsorbent. Further investigations continued in this area with a focus on the use of different adsorbents under wider temperature and pressure conditions as well as with an objective of achieving higher H_2 purity and efficient adsorbent regeneration. Use of dolomite as sorbent[77,83] has been investigated under industrially operated temperature and pressure conditions and H_2 purity from the reactor was found in the range of 92–96%. Various other CO_2 adsorbents include the following: K-promoted hydrotalcite, clay minerals like sepiolite and dolomite, modified double layer hydroxides, spinels with metal oxides, and mixed metal oxides of Mg, La, Ca, etc.[84–88] Yong et al.[89] have recently reviewed the role of activated carbon, zeolites, metal oxides, hydrotalcite compounds, etc. as adsorbents and concluded that activated carbons and zeolites are superior to metal oxides and hydrotalcites for ambient temperature applications. However, metal oxides and hydrotalcites are preferred over activated carbon and zeolites for high-temperature applications. As far as compatibility with SMR is concerned, the K-promoted hydrotalcites exhibit a high and pressure-reversible CO_2 capacity.[90,91] However, this performance is highly dependent on the synthesis and pretreatment of these adsorbents and needs more insights into the fundamental aspects. Double layer hydroxides are also important candidates that are potentially useful for high-temperature PSA processes.[79] There are several other works that report the use of alumina as a high temperature and pressure-reversible CO_2 adsorbent for use in a PSA cycle.[89,92] Lithium zirconate and CaO can also function as high temperature, CO_2 selective adsorbents and have temperature reversibility,[93–96] with reasonable regeneration rates.[97,98] Choice of suitable adsorbent is very important in the overall sorption enhanced steam methane reforming (SESMR) framework. Specifically in an integrated framework, the choice of the adsorbent is very crucial and the capacity of the adsorbent as well as the rate of adsorption are important aspects that govern the overall efficiency of the integrated framework. Future advances in materials engineering will pave way for development of more robust and stable catalytic materials and this is a novel area of research for material scientists.

Various studies have been reported with different degree of complexities in the reactor modeling for SESMR. These essentially involve studies related to parametric sensitivity and optimization for different reactor configurations. Parameters affecting performance of SESMR are temperature, steam-to-carbon ratio, adsorbent to catalyst ratio, etc. Important considerations for SESMR arise from nonlinear adsorption equilibrium and mass transfer limitations on adsorption kinetics. These need to be integrated with the kinetic modeling framework. Ding and Alpay[99] proposed a mathematical model using linear driving force description for mass transfer with incorporation of nonlinear isotherm to describe adsorption, depressurization, and purge steps under nonisobaric as well as nonisothermal conditions. This approach was further extended by Xiu et al.,[100] who carried out numerical investigations for a five-step one-bed sorption enhanced SMR configuration[78] involving adsorption and regeneration by pressure swing adsorption. This model considered component and overall mass balance, pressure drop correlation, energy balance, and adsorption equilibrium isotherm coupled with three chemical reactions for the sorption enhanced cyclic process. This was followed by other numerical investigation[101] for four-step one-bed configuration with three subsections sorption enhanced process with a focus on the effect of subsection temperature on the performance of the SMR. It was established that controlling the subsection temperatures leads to improved SMR performance. Later, this group[102] proposed a detailed mathematical model considering intraparticle diffusion limitations in the modeling framework. This can be considered as the most comprehensive model for SESMR. Such models are, however, computationally very expensive and need model reduction techniques for many applications. Wang and Rodrigues[103] developed a simplified two-section model to decouple the complexity in process modeling and tested it for two reactor dimensions: a lab scale and a pilot scale reactor. Such reduced models are very useful from process control point of view. A dual fluidized bed reactor is another important configuration that has advantage in terms of higher residence time for adsorbent and minimization of attrition of the adsorbent because of low gas velocities. Johnson et al.[104] have carried out numerical investigations for this reactor configuration using a simple two-phase bubbling bed model and established that operation at relatively high-solid circulation rates gives higher system efficiency. The other recent studies include experimental and numerical investigations by Lee et al.[105] and Ochoa-Fernandez et al.[106] These models can be used for optimization and online control to achieve better performance.

One of the important issues in SESMR is the stability of adsorbent. Unstable adsorbents can lead to lower equilibrium hydrogen yields.[107] For fluidized bed operations, resistance to attrition[108] is an important parameter and largely governs the performance of the adsorbant and the process as a whole. The mode used for desorption and its assessment in terms of energy requirement and time of regeneration are also important to achieve better design and performance. High energy requirements for CO_2 desorption can rule out an adsorbent in spite of its better performance in sorption enhancement. The choice of a suitable adsorbent, thus, becomes a trade-off between its effectiveness, stability, regeneration capability, and is a complex issue.

One aspect hindering the performance of multifunctional reactors for SMR is the mass transfer limitations between the catalyst particle and the adsorbent.[11,109] This can be overcome by integrating the catalytic and adsorptive functionalities on a particle level (see Figure 7).[11] This further intensifies the SMR reactor design while at the same time giving an additional degree of freedom in the design of catalyst as well as reactor. Compatibility of adsorption and reaction rates can be facilitated by this kind of design. Some initial study in this regard carried out in our group considering diffusivity inside the particle and particle level characterization (at dif-

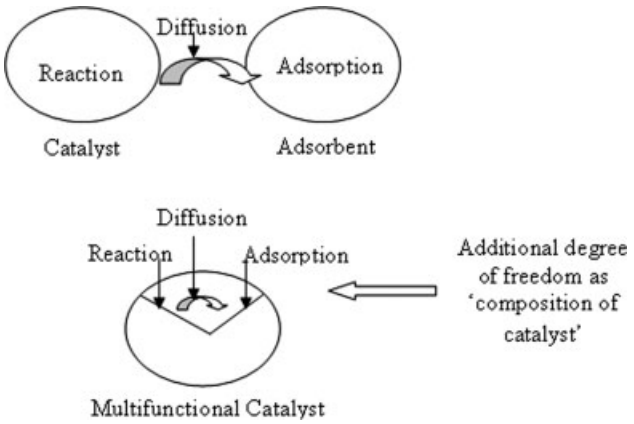

Figure 7. Concept of multifunctional catalyst.

ferent fraction of adsorbent in the multifunctional particle) helps in establishing the operating range for various end use applications such as fuel cell or power generation, etc.[110] This approach is quite generic and can provide rules for selection of the optimum structure of multifunctional catalysts.

As far as future scenario for sorption enhanced SMR is concerned, the major challenge is in the development of appropriate adsorbents and catalysts and their optimal distribution within multifunctional catalyst particle. The design will be facilitated by multiscale modeling framework which will integrate all the events at various scales occurring in SMR. The actual manufacturing of such multifunctional catalysts will, however, require insights into nanoscale design of materials and effective strategies for controlling the distribution of functionalities in the catalyst. This is an emerging area in materials engineering. Thus, novel material developments as well as multiscale modeling hold the key for future progress in SESMR.

Other Efforts in Novel Reactor Design

The main drawback of the SMR reactors is that the temperature gradients in the packed, fluidized, or simulated moving bed configurations can adversely affect the performance resulting in low yield, selectivity, and unsafe operating conditions. Therefore, it is desirable to have compact reactors for efficient operations. Rajashree et al.[111] proposed the concept of tubular packed bed microreactors (TPBM) with catalyst dilution by adsorbent (for sorption enhancement) strategy for SMR. In this configuration, the heat transfer characteristics of the TPBM and the catalyst dilution strategy compliment each other increasing CH_4 conversion and H_2 yield. Other important concept proposed to overcome heat transfer limitations is a catalytic wall reactor[112,113] that consists of a thin wall coated with the same or different catalysts on the two sides. A conventional methane steam reformer is quite large and operates with a contact time of the order of 1 s.[114] Using compact reactors it is possible to get downstream temperatures as low as 200°C, and H_2/CO ratio as high as 42/1 with a residence time of 300 ms at steam/methane ratio of 4/1.[115] In catalytic wall reactors, exothermic reactions occur on one side which supplies heat to endothermic reactions on the other side. This eliminates heat transfer resistance and reduces residence time. The important factors that affect performance of such reactors are stability of the catalyst and the wall material, and heat losses. Various configurations of compact reactors for SMR include a plate-type reformer coupling catalytic combustion and reforming occurring in alternate channels[12], use of heating medium on one side to supply heat to endothermic reaction on the other side.[116] use of catalyst coating to couple catalytic combustion and SMR,[112] concentric tube configuration for efficient heat exchange,[115] a periodically operated two-layer reactor[117] that can produce CO-free hydrogen without any synthesis gas intermediate [very suitable for proton exchange membrane (PEM) fuel cells], etc. Figure 8 shows the schematic of a parallel plate compact reformer.

Gavriilidis et al.,[118] Zanfir and Gavriilidis,[119] and Agar[16] have carried out investigations into coupling multiple functionalities in compact reactors. They reviewed various one and two dimensional approaches to investigate the effect of composition of catalytic functionalities, support material, reactor configuration, and operating conditions on the reactor performance in a generic framework. A detailed insight was, however, provided by Yuan et al.,[120] who employed a three

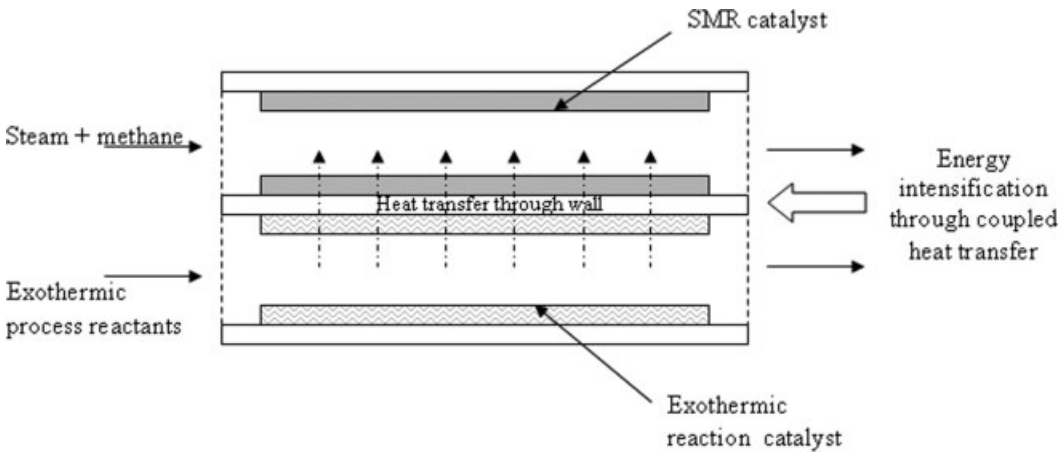

Figure 8. Schematic of a compact plate reformer.

dimensional approach to simulate and analyze compact SMR in a composite domain consisting of a porous active layer, a gas flow duct, and solid plates. It was established that the operating temperature and catalyst loading are the two most important variables affecting the transport processes and reforming reactions, and should be regulated to optimize the performance. Such detailed investigations for different reactor configurations would lead to a more realistic analysis to achieve better process performance. Such models can be used in suitable optimization framework (specifically evolutionary optimization approaches) to arrive at optimum design and operating conditions.

Fuel cell micropower plants are considered to have high exergetic efficiency and have potential to replace rechargeable batteries. As it is difficult to store H_2 in a microsystem, there is demand for onboard production of hydrogen by processing hydrocarbon fuel. This requires investigations into modeling and process integration of PEM fuel cells and its fuel processing sections (SMR, WGS, PROX, and post combustion unit) in order to identify the optimal process flowsheet and operating conditions. Godat and Marechal[121] showed that improvement in energy integration and optimization of operating parameters can lead to increase in the efficiency from 35% to 49%. Such approaches can be used as a basis for the optimal structure determination and the thermoeconomic optimization. Recently, Seo et al.[122] numerically investigated the characteristics of a compact steam reformer with integrated WGS reactor. Their detailed model was used to study the effects of heat transfer and various operating parameters on the reactor performance. It was established that steam/carbon ratio has significant influence on both CH_4 conversion and CO reduction and should be kept at the highest possible value (limited by the cost of steam generation).

A microchannel plant with equal capacity as that of industrial scale plant has been described in the literature based on a contact time below 10 ms (against 1 s for the conventional reactor).[114] Microchannel process technology uses small diameter channel to improve both heat and mass transfer almost by one or two orders of magnitude. These configurations also allow for an increase in the amount of surface per unit volume thus increasing overall productivity per unit volume. The two important variables affecting the performance of microchannel reactors are flow through gap and catalyst thickness.[114] Wall conduction is also an important parameter and hydrogen yield is observed to be the highest for no or very low conductive walls.[123] Stutz et al.[124] numerically investigated the effect of catalyst surface site density and reactor geometry on the performance of a single-channel microreactor. An important conclusion derived from their study was that hydrogen selectivity is dependent on the catalyst loading which is an important degree of freedom to maximize H_2 productivity. Analysis of such complex systems requires three-dimensional models[125] to accurately address the issues related to process performance.

Coupling of catalytic partial oxidation and SMR, oxy steam reforming (OSMR), has also been considered as an alternative route to hydrogen production.[84–86] The use of steam facilitates in converting CO to CO_2, hot-spot minimization, avoid explosion range, and mitigate coke formation.[84–86] Methane conversion for this combined operation is more than the individual process under similar temperature and pressure conditions. Recent developments in OSMR include the experimental investigation by Chen et al.[126] under industrial operating conditions that involved the study of the effect of important operating parameters such as O_2: CH_4 ratio, H_2O: CH_4 ratio, and gas hourly specific velocity on OSMR performance. The important finding was an increase in thermal efficiency from 35.8% to 55.3%. Other important recent contribution is by Barrio et al.[127] who proposed a one-dimensional modeling framework for OSMR and suggested its feasibility for optimization of the process with respect to hot spot minimization. These studies can act as a precursor to better industrial scale design and optimization.

SMR by means of plasma technologies is also an emerging area that provides features such as simplicity, compactness, and quick response to transients.[128] However, use of plasma causes overheating of reaction media and energy inefficiency. Although this renders this process less competitive, a more detailed analysis into the physical and chemical aspects of this process will help in exploring its advantages in the near future.[13] Rusu and Cormier[13] have pioneered in the field of plasma reactors and have carried out experimental and modeling investigations for SMR in rotating discharge reactor. Such configurations can accelerate chemical reactions at low temperatures and with very low energetic costs. Recently, several workers[129,130] have highlighted the applications of plasma materials conversion as a promising technique for energy saving and environmentally safe operation and is attracting the attention of process system engineering (PSE) community.

All these novel configurations for SMR reactors discussed in this article have emerged from the need to achieve energy efficiency, increase hydrogen productivity, and facilitate faster and safer operation. This has been achieved essentially by overcoming the mass and heat transfer and thermodynamic limitations. The most important issue in all these designs is the compatibility of the integrated processes. Figure 9 highlights the strategies for selection of a new integrated process for SMR. A new design has to perform satisfactorily at all the stages of evaluation to be effective as a new SMR design. Detailed modeling investigations in such configurations are required to improve the performance of the existing SMR and pave way for novel intensified configurations. Recently, Sadhukhan and coworkers[131,132] have proposed a methodology to analyze decarbonized energy systems that determine the extent of decarbonization required in energy systems from various objectives such as energy production cost, exergy loss, design constraint, and carbon emission. Such analysis will be of great importance in analyzing various process intensification scenarios for SMRs.

Development of multifunctional catalysts for SMR involving both catalytic and adsorptive functionalities is one of the most promising alternatives to achieve highest level of system integration at the microlevel and overall energy efficiency. In this regard, it is important to focus on the developments in the evolution of catalysts in SMR and various issues thereof. The current SMR catalysts are generally Ni based. However, there are issues of coke formation[7,81] and sulfur poisoning.[81] As the SMR reaction is highly endothermic the reaction requires higher temperatures and more steam to carbon ratio to prevent coking on the catalyst. The

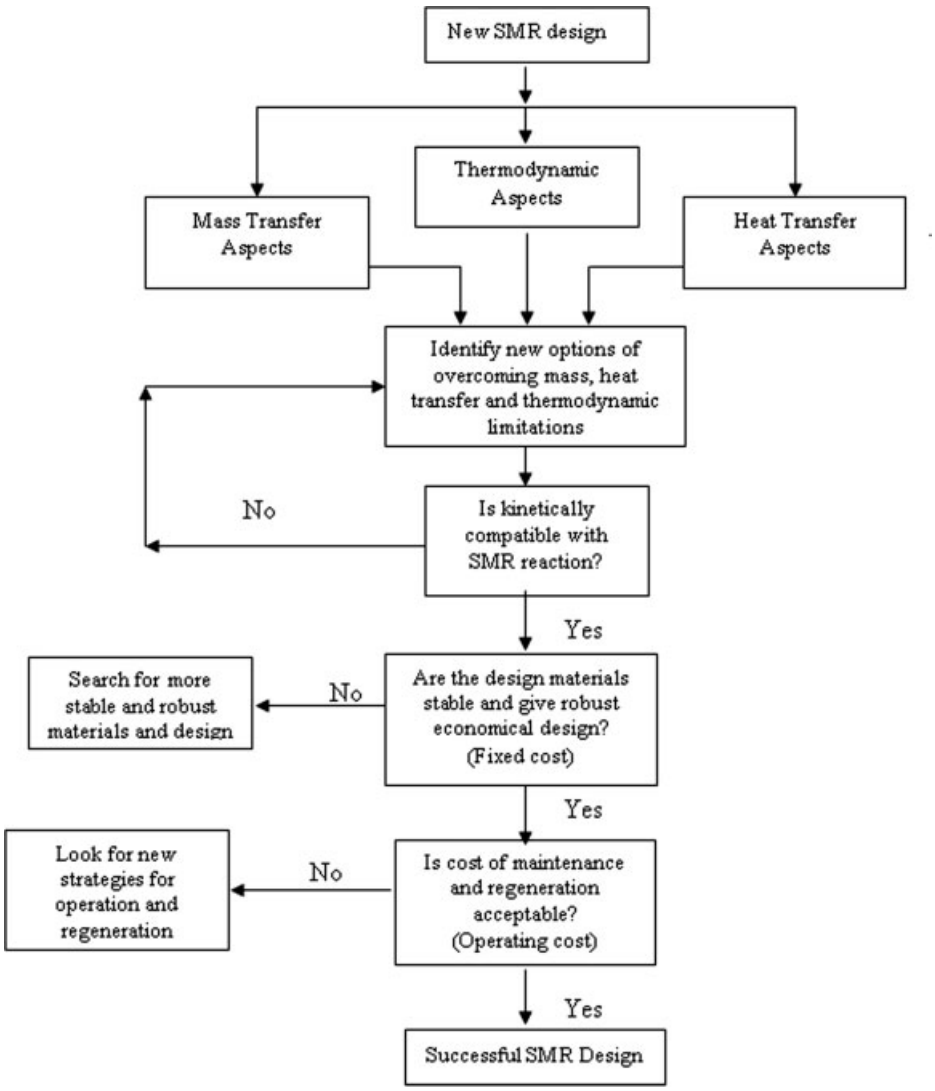

Figure 9. Strategies for assessing novel SMR reactor configurations.

catalysts with high resistance against coking involve Ni catalysts loaded with noble metals such as Au, Pt, Rh, Ru, Pd, and Ir. However, Ni is more suitable from practical point of view because of its low cost, good activity and availability of the know-how. Ni supported by inexpensive thermally stable alumina or alumina–magnesia catalyst is generally an option that is preferred[133] and there are advancements by addition of alkali, alkali earth oxides, and rare earth metal oxides to the alumina support or by using Ni catalyst supported on variety of perovskite-type oxides.[134] Addition of a new adsorptive/reactive functionality will have a great influence on the process and needs to be explored. The phenomena at the molecular level will be greatly influenced by the presence of the adsorptive species and needs to be assessed for its impact on the overall process.

Among the variety of catalysts available for SMR, the optimal choice of the catalyst depends upon the downstream application of the H_2 produced from the reformer. The choice of a suitable catalyst from the library of available materials will involve detailed analysis of the process and is a laborious exercise. This may not always give optimal catalyst for a totally new application. Various existing options include approaches based on combinatorial computational chemistry,[135] CFD,[136] artificial neural network,[137] computer aided data extraction and high throughput experimentation,[138] Monte Carlo simulations with stochastic optimization algorithm,[139] etc., to design novel catalysts. Figure 10 highlights important aspects in catalyst design. These aspects mainly address two most important configurations, structural and functional distributions, related to the catalyst design. Successful catalyst design will involve knowledge extraction from available resources to design new catalysts or improve the performance of the existing catalysts. This is an emerging area of research.

Summary of Intensification Approaches in SMR Technologies

Intensification in SMR technology will involve integration in both modeling as well as process aspects. The key to

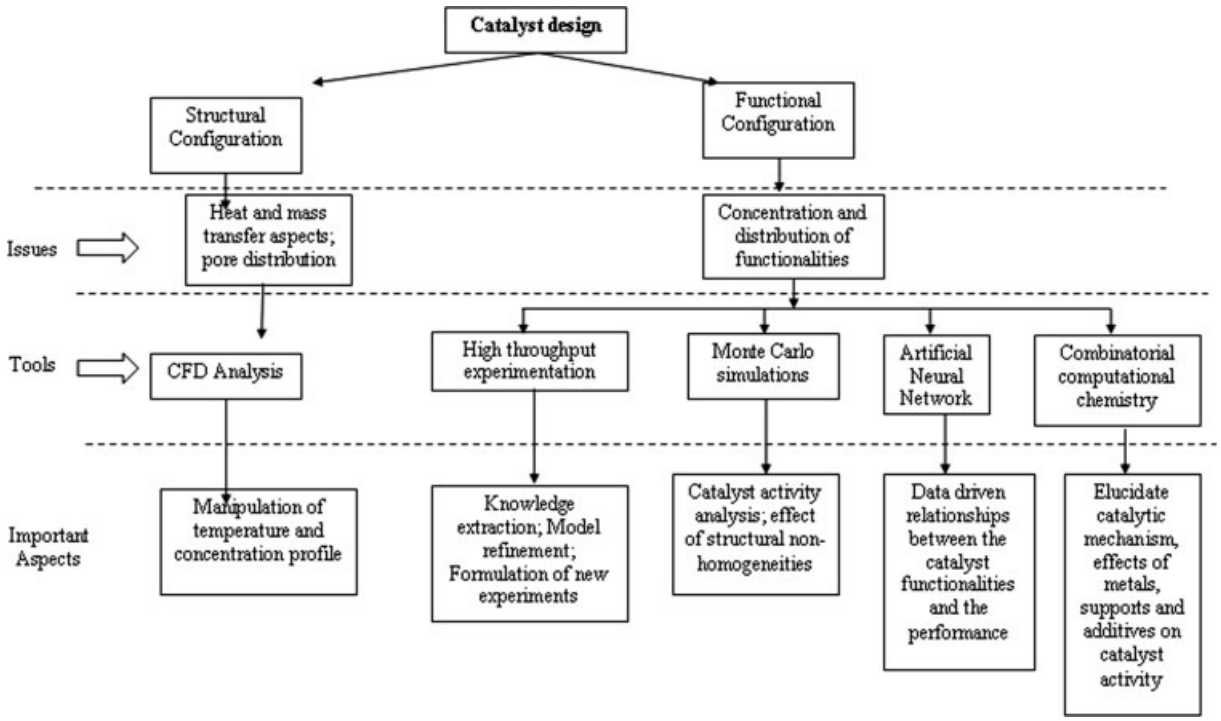

Figure 10. Important aspects in catalyst design.

model intensification lies in multiscale modeling approaches while the key to process intensification lies in innovating ways for overcoming mass and heat transfer and thermodynamic limitations. For multiscale modeling, determination of reaction kinetics for SMR from molecular consideration is, therefore, important. The kinetic mechanism of the SMR depends on the type of the catalysts and support used and the composition of the catalyst. Detailed microkinetic modeling of these systems have proved to be helpful to build rigorous models that can be used to optimize the performance of SMR. This analysis at microscopic scale needs to be integrated with the macroscopic reactor scale through mesoscale approaches involving catalytic surface events. Feedback between these three domains is important to achieve overall system performance by identifying and targeting important parameters at all the scales. Advances in multiscale modeling and simulation have been limited till now due to unavailability of the better computational resources. This problem will be less significant in the future as many high-speed computational frameworks are becoming available now and this will lead to the development of more generic and robust framework for SMR.

As far as integration of SMR with other processes is concerned, the compatibility between the two processes, suitable material selection, stability, robustness, maintenance, regeneration, and operating modes are important issues. Research in the area of membrane reactors is required toward the development of more thermally and mechanically stable membranes as well as membrane supports. The challenge from operation point of view is the minimization of energy and surface area of the membrane modules. CFD assisted detailed model of the membrane reactors have recently been incorporated and advances in these will assist in understanding the detailed transport and kinetic aspects and will help in better design. The cost and maintenance of membranes is still a concern and further developments in materials engineering will pave way for better membrane designs. For sorption enhanced processes, development of multifunctional catalysis is still a primitive area, both computationally as well as experimentally. The approaches based on microkinetic modeling and Monte Carlo simulations can be used to arrive at the design of the catalysts. This will involve modeling of catalyst particle as well as reactor considering diffusional limitations and incorporating kinetic mechanism derived from microkinetic modeling and subsequent optimization of various parameters such as size of the catalyst pellet, volume fraction of the catalyst and adsorbent, and the structural arrangement within the particle. Other important aspects in SESMR are development of better adsorptive materials, efficient strategies for regeneration and coupling with various pre and postprocesses.

Development in compact reactor configuration has been triggered by possible application of SMR for fuel cell application. Efficient process analysis and development of thermally stable materials are important aspects in the development of various compact reformers. Future advances will arise from the use of more detailed transport and kinetic models for process analysis and subsequent use of these models for process optimization and control.

To summarize, computational catalyst design and optimization, development of more detailed and rigorous models considering multiscale modeling framework, and development of novel intensified reactor configurations by exploring new avenues for overcoming mass and heat transfer, and thermodynamic limitations are the three important objectives for the future research. The analysis of SMR keeping in

mind the future requirements, such as carbon capture and sequestration and integrated approaches considering the downstream application such as fuel cells, power plants, upgrading, etc., is important.

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