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Decentralized production of hydrogen for residential PEM fuel cells from piped natural gas by low temperature steam-methane reforming using sorption enhanced reaction concept

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Background

Decentralized generation of small-scale stationary power (< 250 KW) for residential or commercial use has been a subject of much interest during the last decade and many corporations around the world have engaged in research and development of fuel cell technology for this application [1–10]. The driver for this technology is rapidly expanding worldwide demand for more heating, cooling and electrical supply by increasing populations and growing economics [1, 2, 4, 8]. Some of the potential benefits include (a) quiet and reliable operation, (b) power on demand, (c) efficiency at low load, (d) higher efficiency vis a vis combustion route of power generation, (e) lower CO_2 production than combustion, (f) absence of transmission line loss, and (f) absence of SO_x and NO_x production at the point of operation.

Proton Exchange Membrane (PEM) Fuel Cell

Proton exchange membrane or polymer electrolyte membrane (PEM) fuel cell technology which transforms the chemical energy liberated during the electrochemical reaction between hydrogen and oxygen to electric energy as opposed to direct combustion of hydrogen and oxygen to produce thermal energy has attracted most attention [11 - 13].

Some of the attractive features of the PEM fuel cells include (a) delivery of high power density, (b) light weight and compactness, (c) relatively low temperature operation (~ 60-80°C), (d) use of non-corrosive electrolyte (e) quick start-up, (f) rapid response to demand changes in power, (g) elimination of storage battery, and (h) durability [2, 12, 13].
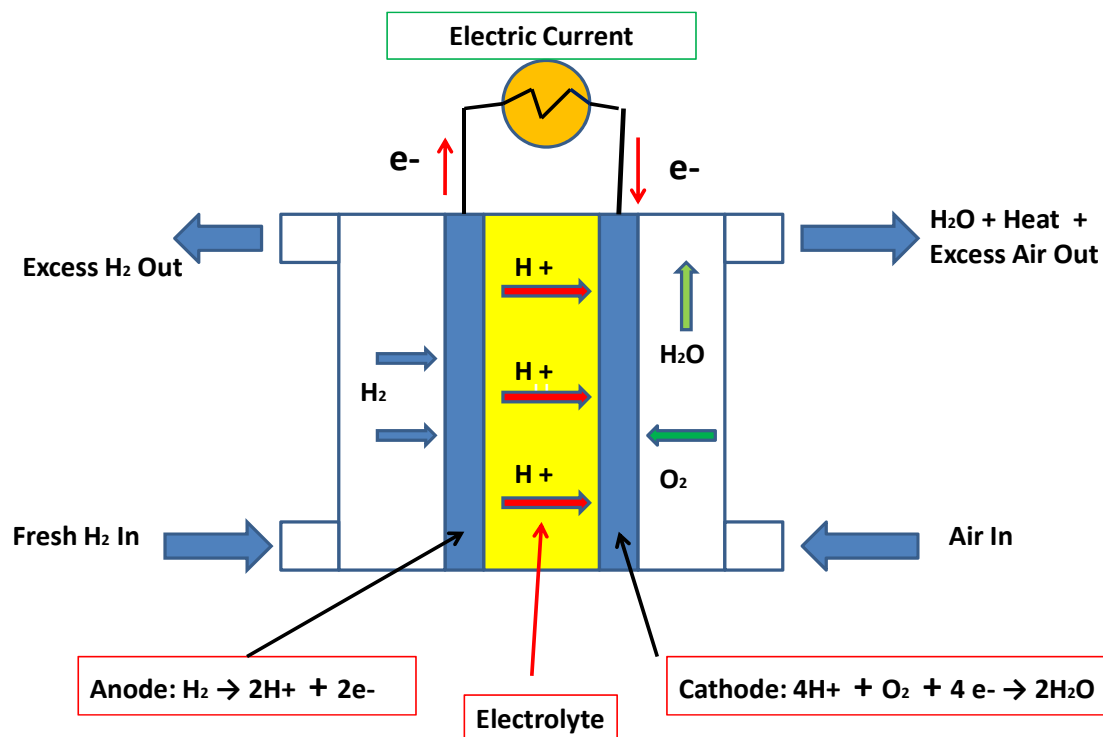
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Fig. 1. Cartoon of a hydrogen PEM fuel cell.

Figure 1 is a cartoon depicting the principle of operation of a hydrogen PEM fuel cell [11]. It uses a solid polymer as an electrolyte and porous carbon electrodes containing primarily a platinum catalyst. The most commonly used membrane is humidified Nafion developed by DuPont Corp. The fuel cell needs pure hydrogen, oxygen (from air) and water (to moisten the membrane) for operation. H_2 is catalytically dissociated into a proton and an electron at the anode followed by selective transport of only the proton through the membrane to the cathode, where it reacts with dissociated O_2 to produce H_2O and heat. The relevant chemical reactions at the electrodes are shown in the figure. The net reaction ($2H_2 + O_2 \leftrightarrow 2H_2O$) is highly exothermic which generates a large amount of heat in the fuel cell. The free electron released at the anode moves to the cathode through an external circuit, thereby, generating electric current.

The purities of H_2 and O_2 used in the PEM hydrogen fuel cell are critical issues. The catalytic activity of the platinum electrodes in a PEM fuel cell is poisoned by the presence of trace amounts of CO, NH_3, H_2S and HCN in the H_2 [4, 11, 14], as well as by the presence of trace amounts of SO_2 and H_2S in the O_2 (air) [15]. Presence of CH_4 in the H_2 is regarded to be inert towards the performance of the electrodes. CO_2 itself is also regarded to be inert, but the formation of trace CO by reverse water gas shift reaction (RWGS) at the anode [$CO_2 + H_2 \leftrightarrow CO + H_2O$] due to the presence of CO_2 in H_2 can have the same detrimental effect as in the presence of trace CO in H_2 [14].

Figure 2 shows thermodynamic estimation of CO formation by reaction between CO_2 and H_2 at different temperatures of operation of a PEM fuel cell [14]. It may be seen that a considerable amount of CO, albeit in parts per million level, is formed at the anode which is sufficient to poison the catalyst by being selectively chemisorbed on the platinum electrode over H_2.
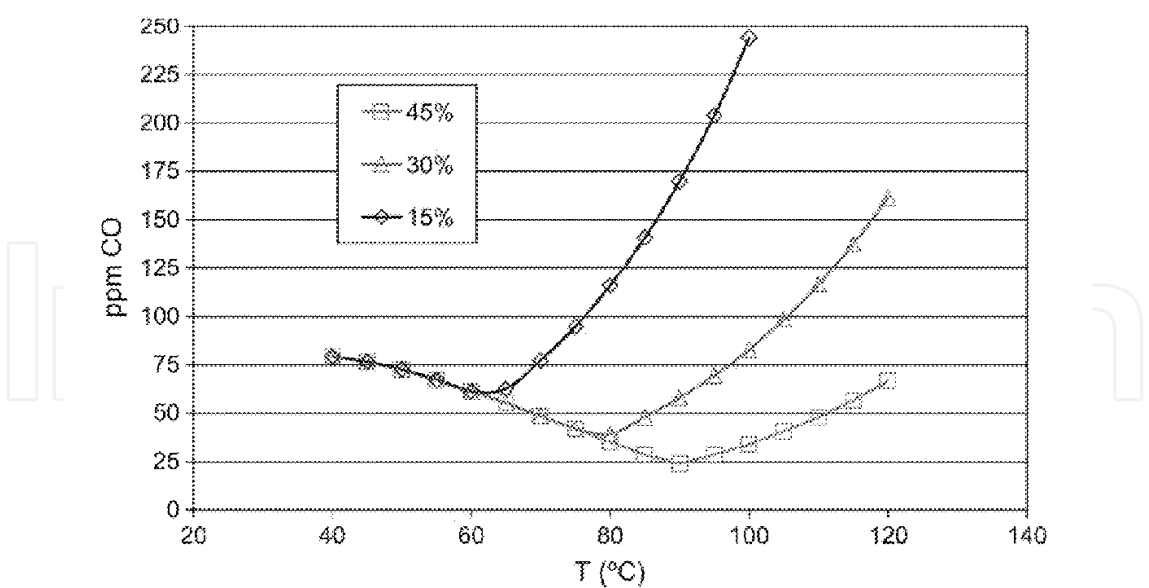
Fig. 2. Equilibrium concentration of CO produced by RWGS reaction from a feed gas containing
3:1 H_2: CO_2 at 1.5 bar and different temperatures in presence of different concentrations of water.
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Figures 3 and 4, respectively, show two sets of experimental data demonstrating the detrimental
performance of a PEM fuel cell in presence of bulk CO_2 in H_2 [14] and trace SO_2 in air [15].

Figure 3 shows that the cell voltage for a given current density decreases as the CO_2
concentration in the feed H_2 increases. Figure 4 shows that the normalized output voltage of
a fuel cell decreases with operation time when the air introduced at the cathode is
contaminated with even a trace amount (<1.5 ppm) of SO_2. The rate of degradation of the
cell performance increases rapidly as the concentration of contaminated SO_2 is increased.
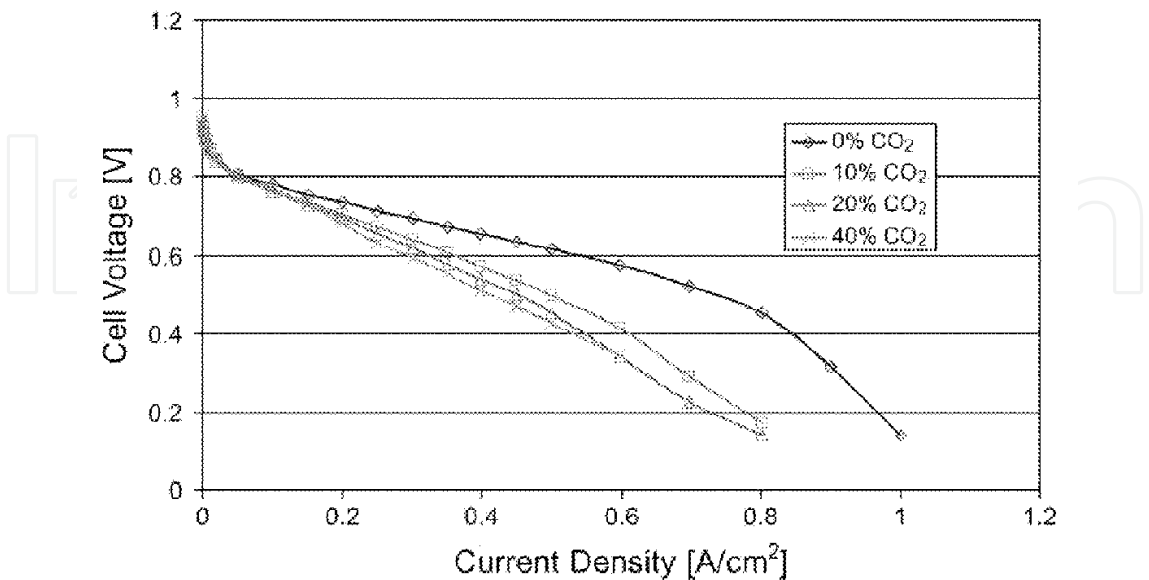

Fig. 3. Polarization curves of a Nafion fuel cell at various CO_2 concentrations in the feed H_2
at 65°C. P = 1.5 atm. Reprinted from J. Power Sources, 110, 117-124 (2002) with permission
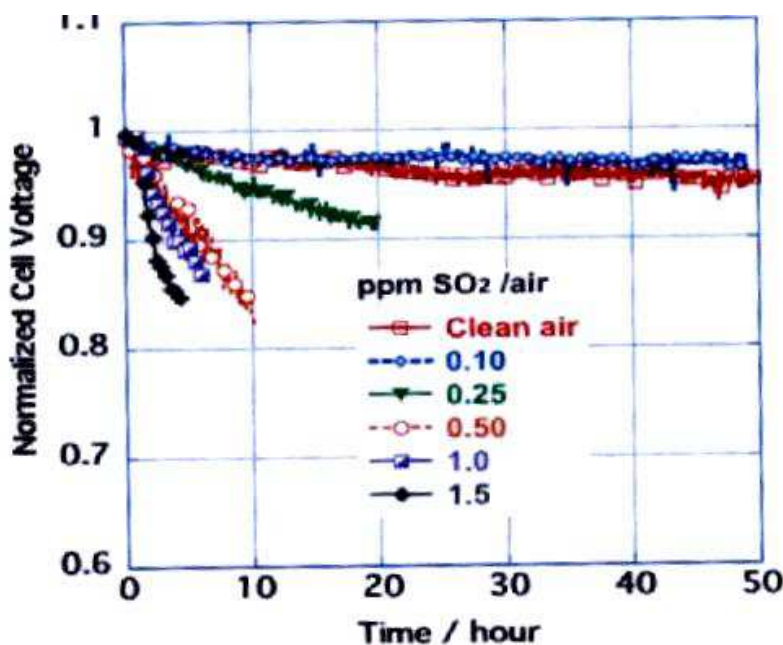from Elsevier.

Fig. 4. Effect of the presence of trace SO_2 in air at the cathode of a PEM fuel cell.

Consequently, essentially CO_x, sulfur, and NH_3 free H_2 and air streams are needed as feed gases for efficient and durable operation of a PEM fuel cell. A 2005 draft specification of the fuel cell grade hydrogen suggested by the U. S. Department of Energy is provided in Table 1 [15].

Components	Levels
Hydrogen	>99,9 %
CO	~0.1 ppm
CO_2	~5.0 ppm
NH_3	~1 ppm
Non CH_4 hydrocarbons	~100 ppm

Table 1. Suggested specification of H_2 purity for PEM fuel cell [15].

This requirement of very high purity H_2 may be a potential limitation of the use of a PEM fuel cell for residential use. It should, however, be noted that a very active R & D effort is being carried out to produce more CO_x tolerant anode catalysts by employing platinum-ruthenium catalysts made by different preparation methods as well as by using other catalyst formulations [16 - 21]. The other potential limitations of commercializing residential fuel cells may be (a) high manufacturing costs, (b) complex heat and water management issues, (c) long warm up period, (d) inferior performance when cold, and (e) membrane life and cost of replacement [12].

Natural Gas as source of Hydrogen

The high purity H_2 required by a PEM fuel cell must be easily available at the point of location of residential use. One potential solution is to directly produce fuel-cell grade H_2 at the site of the fuel cell by steam reforming of methane [22]. A network of pipe lines to

supply natural gas for domestic (heating or cooking), and commercial (heating) applications already exists in the infrastructure of many advanced countries. The gas is typically available at a pressure of 2 – 60 psig, and is centrally processed to remove impurities like H_2O, CO_2, S, He, and heavy hydrocarbons.
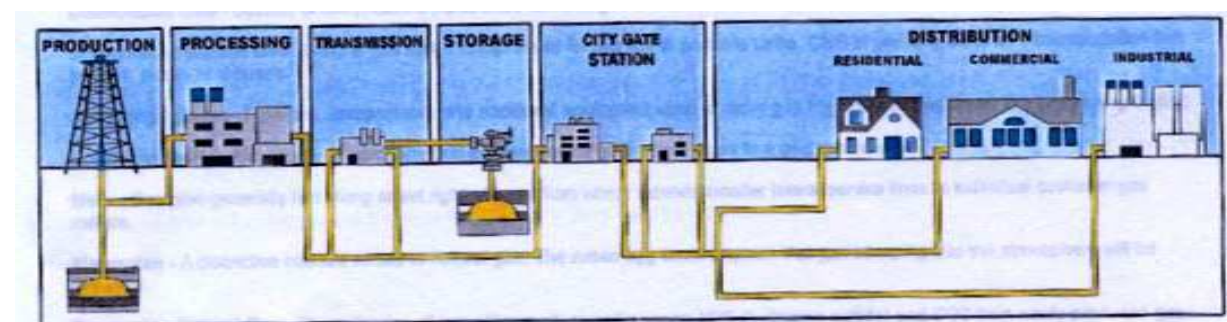
Fig. 5. Lay-out of infrastructure for natural gas supply.

Figure 5 shows a cartoon of a typical infrastructure lay-out for natural gas production, processing (impurity removal), transmission, storage, and distribution [23]. The gas leaves the transmission system and enters the distribution system at the city gate stations where it may be odorized by adding trace amounts of mercaptans as a safety measure for domestic use.

Production of Fuel Cell Grade H_2 from Natural Gas

Catalytic reformation of CH_4 by reaction with steam is the most efficient and economically viable route of production of H_2 and many commercial processes employing this principle have been developed [24]. The primary reactions in the reforming reactor are:

- Endothermic steam-methane reforming (SMR) reaction :
  $$CH_4 + H_2O \leftrightarrow CO + 3H_2; \quad \Delta H_R = +206 \text{ kJ/mole} \tag{1}$$
- Exothermic water gas shift (WGS) reaction :
  $$CO + H_2O \leftrightarrow CO_2 + H_2; \quad \Delta H_R = -41 \text{ kJ/mole} \tag{2}$$
- Endothermic net reaction :
  $$CH_4 + 2 H_2O \leftrightarrow CO_2 + 4H_2; \Delta H_R = +165 \text{ kJ/mole} \tag{3}$$

These reactions are controlled by the chemical thermodynamic equilibria, which dictate the preferred reaction conditions (pressure, temperature and feed $H_2O:CH_4$ ratio), the H_2 conversion, and the composition of the SMR reaction product gas containing $H_2 + CO_2$ (bulk) + CO (dilute) + CH_4 (dilute) on a dry basis.

Figure 6 shows the equilibrium constants for the reversible SMR (K_{SMR}) and WGS (K_{WGS}) reactions [25], and the estimated thermodynamic conversion of CH_4 to H_2 by SMR as a function of reaction temperature (reactor pressure = 1.5 atm, feed H_2O/CH_4 ratio = 5:1). It may be seen that the maximum conversion (~90%) of CH_4 to H_2 can be achieved at a reaction temperature of ~700 – 800°C. Such high temperature requires expensive metallurgy for reactor construction, and a rather complex system of heat management. Table 2 shows the equilibrium compositions of the SMR reactor gas at different operating temperatures for a reactor feed gas containing 5:1 $H_2O:CH_4$ at 1.5 atm. It shows that the reactor effluent gas must be stringently purified in order to produce a stream of pure H_2.
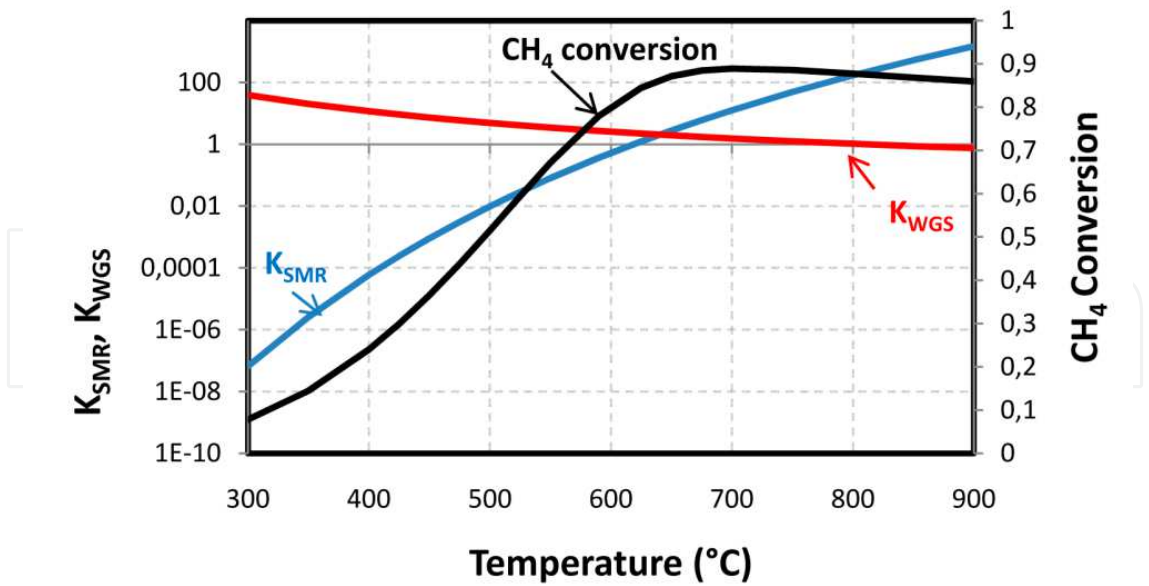
Fig. 6. Reaction equilibrium constants and thermodynamic CH_4 to H_2 conversion for SMR reaction.

Reaction Temperature (C)	Reactor effluent gas composition (dry basis) (mole %)			
	CO_2	CO	CH_4	H_2
800	11.39	10.75	0.03	77.83
700	13.18	8.45	0.32	78.06
590	15.41	4.70	4.18	75.71
550	15.87	3.11	8.15	72.87
520	15.89	2.09	12.21	69.82

Table 2. Equilibrium compositions of SMR reactor effluent gases.

Conventional Process Scheme for H_2 Production by SMR [24]

The most common commercial method for production of high purity H_2 (99.999+ %) from natural gas for fuel cell use consists of high temperature (~800 -900°C) catalytic steam-methane reforming (SMR), followed by catalytic water gas shifting (WGS) of the reaction products at ~ 300 – 400°C, and finally purification of the WGS reactor effluent gas to produce pure H_2 at feed gas pressure by employing a multi-step, multi column, pressure swing adsorption (PSA) process [24]. The feed natural gas to the process is pre-treated to remove trace S and N impurities, if needed. The PSA process is operated at a near ambient temperature (20 -40°C) by employing physi-sorbents like zeolites, aluminas, and activated carbons for removal of the impurities (H_2O, CO_2, CO, CH_4, N_2) from the H_2 product gas. The feed gas to the PSA system typically contains 15 – 25 % CO_2 + 1 – 4 % CO + 1 – 5 % CH_4 + 0.2% N_2 in H_2 (dry basis). A waste gas containing all of the carbon impurities and un- recovered hydrogen is also produced by the PSA system which is used as fuel in the SMR furnace.

Figure 7 shows a simplified box diagram of the process for production of ultra pure H_2 from natural gas by the conventional SMR-WGS-PSA route.
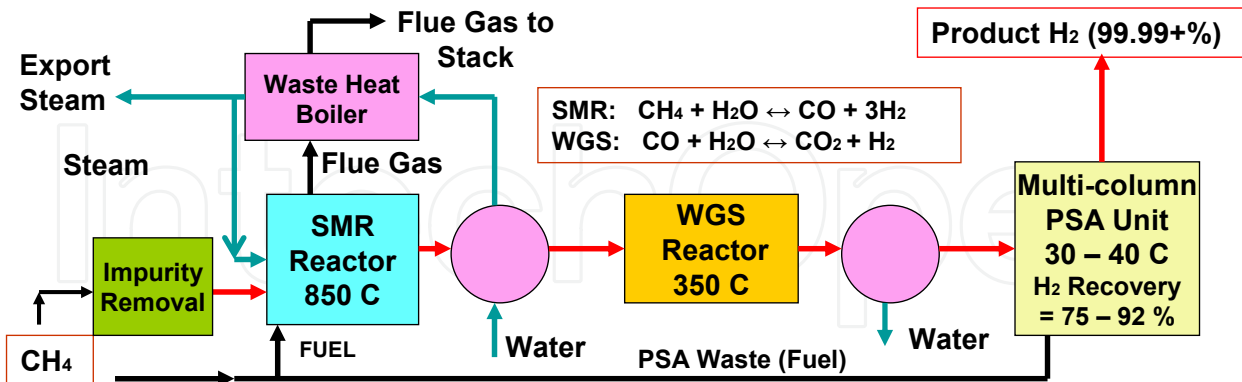

Fig. 7. Conventional steam-methane reforming route of H_2 production from natural gas.

Although the scheme shown by Figure 7 has become the state of the art technology for production of ~ 1 to 150 MMSCFD of H_2 from CH_4, there are several unattractive but unavoidable features for scaling down the process for residential fuel cell use (H_2 demand for a 250 kW PEM fuel cell is only ~0.15 MMSCFD). These include (a) operation of the SMR reactor at high temperature, (b) use of a part of the purified H_2 product (8 -25%) to regenerate the PSA adsorbents by purge, thereby reducing the over-all recovery of H_2 produced by the SMR and WGS reactions, (c) generation of export steam in order to recover the excess heat required for the operation of the relatively low efficiency SMR reactor, and (d) fairly complex nature of the process using several unit operations which requires large footprint and capital cost.

Alternative Process Scheme for H_2 production by SMR [1, 26]

An alternative process scheme has been developed for production of fuel cell grade H_2 from CH_4 by SMR [1, 26]. It replaces the PSA purification step of the conventional scheme of Figure 7 by a catalytic PROX /SELOX (Preferential/ Selective Oxidation) reactor which selectively oxidizes the residual CO (~ 1 - 4 %) from the WGS reactor effluent gas to CO_2 ($CO + 0.5 O_2 \rightarrow CO_2$) in presence of excess H_2 at a moderate temperature of 80 – 200°C. A small quantity of air is added to the PROX reactor feed to supply the oxygen needed for this purpose. The CO level can be reduced to ~ 10 ppm by the PROX concept. Figure 8 is a schematic box diagram for this approach.
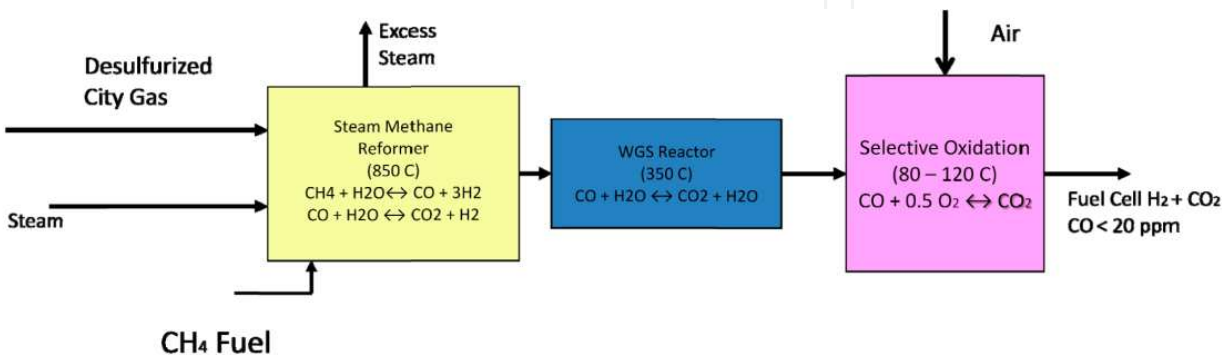

Fig. 8. Alternative steam-methane reforming route of H_2 production from natural gas.

Selectivity of CO oxidation to produce CO_2 vis a vis H_2 oxidation to produce H_2O, and the absolute conversion of CO to CO_2 are two critical performance markers for the PROX catalyst. A large volume of research on mono- and bi- metallic PROX catalyst formulation, nature of support matrix, and method of preparation has been published, and the subject is an active area of research around the world [27 - 38]. The common catalysts include noble metals (Pt, Ru, Rh, Pd) supported on a porous matrix such as alumina [32, 38]. Some of them offer good catalytic activity (~ 100 % CO conversion with 30 - 50 % selectivity) in the temperature range of 130 – 200°C.

The performance of a PROX catalyst may substantially deteriorate in the presence of H_2O and CO_2. Figure 9 shows an example where both the CO conversion (solid lines) and selectivity (dashed lines) of a PROX catalyst [1% (1:1) Pt Au/CeO_2 produced by single step-sol-gel method] decrease substantially in presence of CO_2 in the reactant gas (1% CO, 1% O_2, 0 – 25 % CO_2, 40 % H_2 and balance He) at all temperatures [37].

Figure 10 shows another example of the performance of a PROX catalyst (Pt/FAU) at a temperature of 165°C where the CO conversion and selectivity were not affected by the presence of CO_2 and H_2O in a long term stability test [38]. The reactant for this test contained 1.21 % CO, 2.9 % H_2O, 25.25 % CO_2 and 70.63 % H_2.
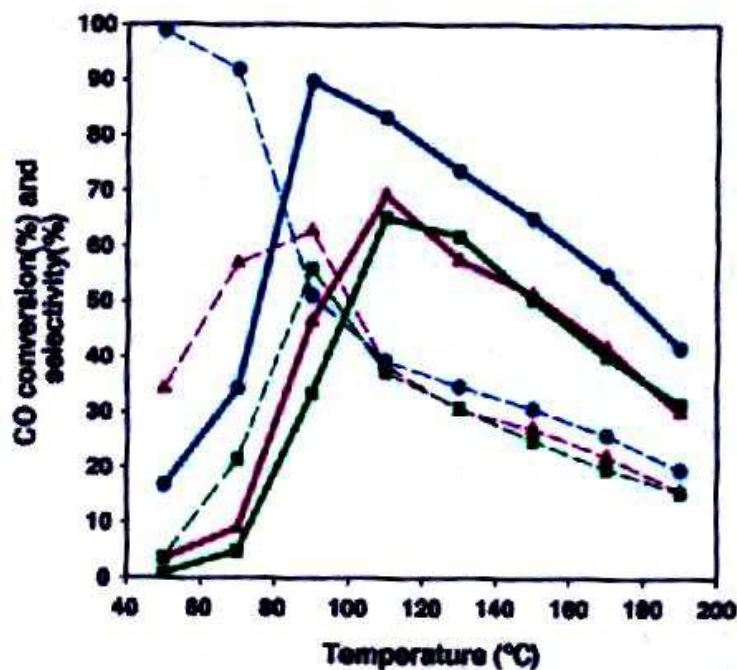

Fig. 9. Effect of CO_2 in feed gas on performance of a PROX catalyst.
● 0 % CO_2, Δ 5 % CO_2 □ 25 % CO_2
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Clearly, a practical PROX catalyst for producing an essentially CO free H_2 for fuel cell application must exhibit ~ 100 % CO conversion in presence of CO_2 and H_2O. Less than 100 % CO oxidation selectivity may be acceptable albeit with the loss of some H_2 produced by SMR. The presence of CO_2 in the effluent gas from a PROX reactor, however, can be the cause of anode deactivation of a PEM fuel cell due to reformation of CO by RWGS reaction as discussed earlier.
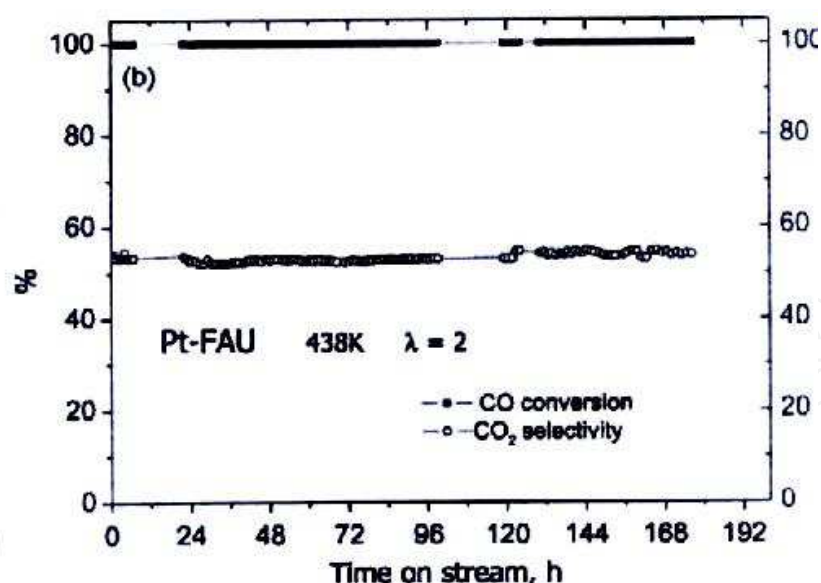
Fig. 10. Performance of Pt/Fau PROX catalyst. Reprinted from Applied Catalysis A;
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Sorption Enhanced Reaction (SER) Concepts for H_2 Production by Low Temperature SMR

Recently, several novel adsorptive process concepts called 'sorption enhanced reaction (SER)' have been designed to substantially enhance the performance of SMR and WGS reactors for production of fuel cell grade H_2 from CH_4 by circumventing the thermodynamic limitations of these reactions. The key benefits include:

- Drastically increase the H_2 product purity and conversion in a single unit operation
- Significantly lower the SMR reaction temperature without sacrificing process performance
- Enhance the kinetics of the forward SMR reaction
- Increase the over-all H_2 recovery from the plant
- Reduce the plant foot print and cost by integration of the reactors
  (SMR and WGS) and the PSA unit as a single unit operation, and by lowering the temperature of SMR reaction (easier heat management and loss).

These advantages are achieved by applying the Le Chatelier's principle, whereby one of the reaction products, CO_2, is selectively removed from the reaction zone at the reaction temperature. An admixture of a reversible CO_2 chemisorbent, which can selectively sorb CO_2 in presence of steam at the reaction temperature, and an SMR catalyst is used in the sorber-reactor for this purpose. The chemisorbent is periodically regenerated for re-use by desorbing the CO_2 using the principles of pressure swing adsorption (PSA) or thermal swing adsorption (TSA) processes.

A recent monograph entitled 'Sorption Enhanced Reaction Concepts for Hydrogen Production: Materials and Processes' [39] and a review article entitled 'Reversible Chemisorbents for CO_2 and their Potential Applications' [40] describe the current state of the art on the SER processes for H_2 production by SMR and the CO_2 chemisorbents used in them. Chemisorbents utilizing either bulk (e.g. CaO) or surface (e.g. K_2CO_3 promoted

hydrotalcite) reactions with CO_2 have been used in these processes [39, 40]. Fixed bed sorber-reactors using both types of chemisorbents have been considered by most authors [39], while a fluidized bed sorber- reactor using the first type of chemisorbent has been evaluated by Harrison [39, 41].
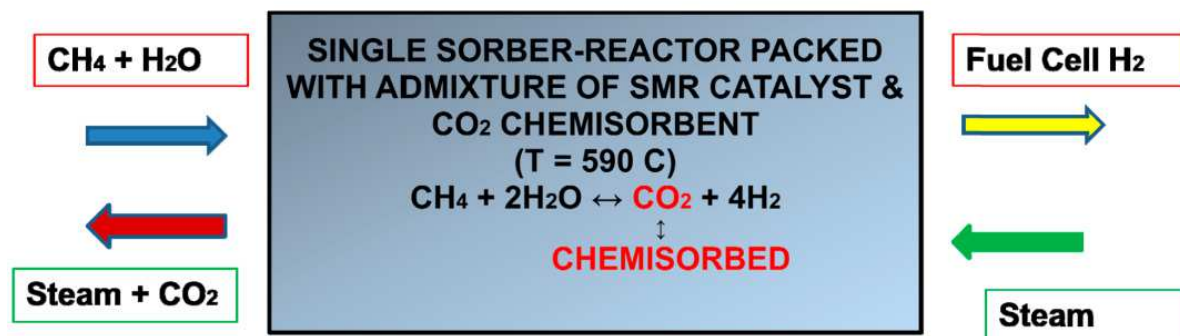
| CH₄ + H₂O | SINGLE SORBER-REACTOR PACKED WITH ADMIXTURE OF SMR CATALYST & CO₂ CHEMISORBENT (T = 590 C) CH₄ + 2H₂O ↔ CO₂ + 4H₂ ↕ CHEMISORBED | Fuel Cell H₂ |

Fig. 11. Conceptual sketch of SER SMR process concepts.

A fixed- bed cyclic SER process employing a CO_2 chemisorbent utilizing surface reaction may be preferred for the residential fuel cell application because of (a) direct production of high purity H_2 by SMR with high conversion of CH_4 to H_2, (b) relatively lower temperature of operation, (c) ease of CO_2 regeneration using conventional principles of pressure or thermal swing adsorption processes , (d) use of steam purge for CO_2 desorption, (e) process compactness, (f) faster chemisorption kinetics, and (g) absence of sorbent transportation. Figure 11 is a conceptual drawing of a generic fixed-bed SER process concept for directly producing fuel cell grade H_2 by low temperature SMR.

Surface reaction based CO_2 chemisorbent used in SER processes for H_2 production by SMR

K_2CO_3 promoted hydrotalcite has been found to be an acceptable CO_2 chemisorbent for fixed-bed adsorptive SER processes (PSA or TSA) operated at a temperature of 400 – 550°C for production of fuel cell grade H_2 by SMR [40, 42] because it provides (i) a decent cyclic CO_2 working capacity under a pressure or thermal swing mode of SER process operation, (ii) fast CO_2 chemisorption kinetics, (iii) moderate isosteric heat of CO_2 sorption, (iv) nearly infinite selectivity of sorption for CO_2 in presence of steam, CO, CH_4 and H_2, (v) relatively easy desorption of CO_2 by purge using steam, and (vi) thermal stability. Some of the key relevant characteristics of CO_2 chemisorption on the material are described below:

Chemisorption Equilibria [40, 42]:
Figure 12 shows the equilibrium CO_2 chemisorption isotherms on a sample of the promoted hydrotalcite at different temperatures. An analytical isotherm model incorporating simultaneous Langmuirian surface chemisorption and an additional surface reaction between the chemisorbed and gaseous CO_2 molecules describes the isotherms adequately (lines in Figure 12). The heats of these reactions are moderate, being respectively, 5.0 and 10.1 Kcal/mole.

Mass transfer rate for CO_2 chemisorption [40, 42, 53]:
The conventional linear driving force (LDF) model was found to adequately describe the over-all mass transfer of CO_2 on promoted hydrotalcite [40].The same LDF mass transfer coefficient (k) described both sorption and desorption of CO_2. Figure 13 shows the temperature coefficient of k [40, 53]. The activation energy for k was 4.5 Kcal/mole.
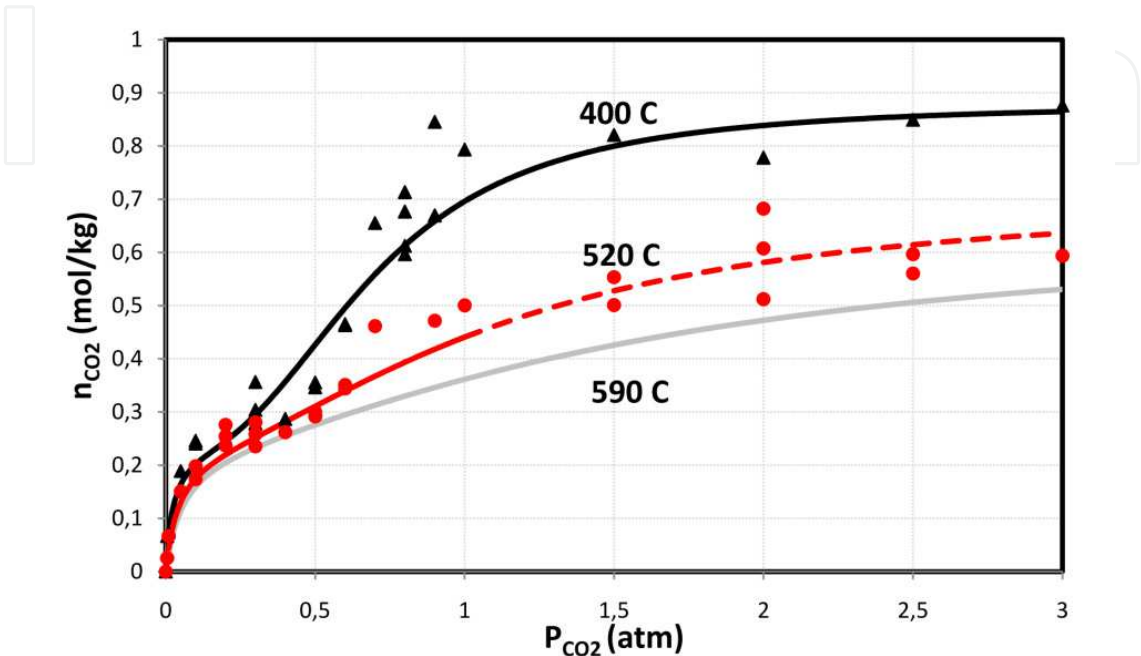

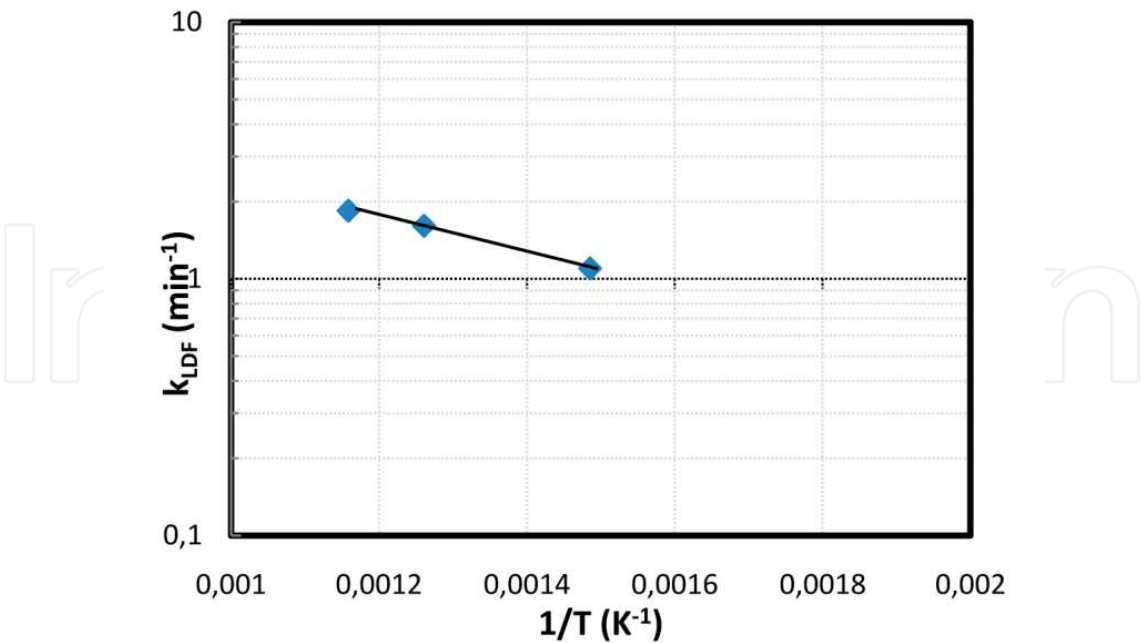Fig. 12. Chemisorption isotherms of CO_2 on K_2CO_3 promoted hydrotalcite.

Fig. 13. Temperature dependence of CO_2 mass transfer coefficient on K_2CO_3 promoted hydrotalcite.

Experimental demonstration of SER-SMR concept [53]:
Figure 14 experimentally demonstrates the SER concept using a packed column (63.4 cm long) of a 2:1 admixture of K_2CO_3 promoted hydrotalcite and a commercial Ni/Al_2O_3 SMR catalyst (Sud Chemie Corp.). A pre-heated feed gas mixture containing ~37 mole % H_2O + 7.4 mole % CH_4 + Ar was passed through the column at near ambient pressure. The column was initially heated to 550°C and filled with Ar.
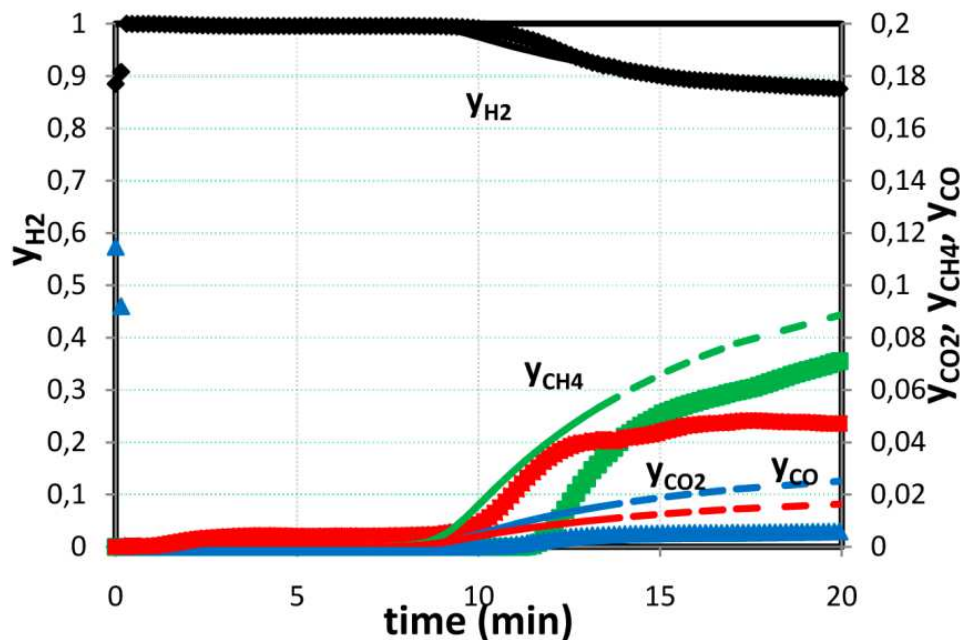

Fig. 14. Experimental demonstration of SER- SMR concept at 550°C using promoted hydrotalcite.

It may be seen from Figure 14 that the effluent gas from the sorber- reactor (solid lines) contained a stream of high purity H_2 (CO_x < 20 ppm) which was suitable for use in a H_2 fuel cell for a period of time. Thereafter, CO, CH_4, and CO_2 simultaneously broke through the sorber-reactor and their mole fractions rapidly rose to different plateau levels which corresponded to the thermodynamic reaction product concentrations of the SMR reaction (without the chemisorbent) at the reaction temperature. The average CH_4 mole fraction of the high purity H_2 product stream was 0.35 mole %. The conversion of feed CH_4 to pure H_2 product was 98.6 %. The dashed lines in the Figure are simulated performance using a model [53].

Pressure swing sorption enhanced reaction (PSSER) process

A pressure swing sorption enhanced reaction (PSSER) process for low temperature (~500 °C) SMR was designed by Sircar and coworkers [43, 44]. The process employed a pair of fixed bed sorber-reactors and it could directly produce a fuel-cell grade H_2 using K_2CO_3 promoted hydrotalcite as the CO_2 chemisorbent in the process. The sorbent was periodically regenerated by purging it with steam at the reaction temperature under a sub-atmospheric pressure condition. The cyclic process consisted of four steps: (a) sorption –reaction at a super-ambient pressure to produce the fuel-cell grade H_2 product at feed gas pressure, (b)

counter-current depressurization to near ambient pressure, (c) counter-current steam purge at sub-atmospheric pressure, and (d) counter-current pressurization with steam to feed pressure. These PSSER process steps were operated under a nearly isothermal condition.

A shell and tube reactor design was suggested for the above-described PSSER process. Two different types of indirect heat transfer methods were also proposed for supplying the endothermic heat of SMR reaction and heat for CO_2 desorption. They consisted of (a) flowing a vaporized heat transfer liquid through the shell side of the reactor so that the condensing vapor would supply the heat of reaction in the reactor and maintain a constant reactor temperature during all steps of the process, and (b) indirect gas heating (IGH) by flowing a hot flue gas through the shell side of the reactor with finned tubes to supply the heat of reaction [43].

Figure 15 is a schematic flow diagram of a two column PSSER system for production of H_2. An example of the cyclic steady state performance of the PSSER process from a pilot scale test apparatus is given in Table 3 which shows that fuel-cell grade H_2 with high CH_4 to H_2 conversion can be achieved by the process. Sircar and co-workers also proposed that the performance of the PSSER process could be improved by (a) use of a catalyst only section in the feed end of the sorber-reactor, (b) using a dilute amount of H_2 with the purge steam, and (c) imposing a moderately increasing temperature gradient from the feed to the product end of the sorber-reactor [45].
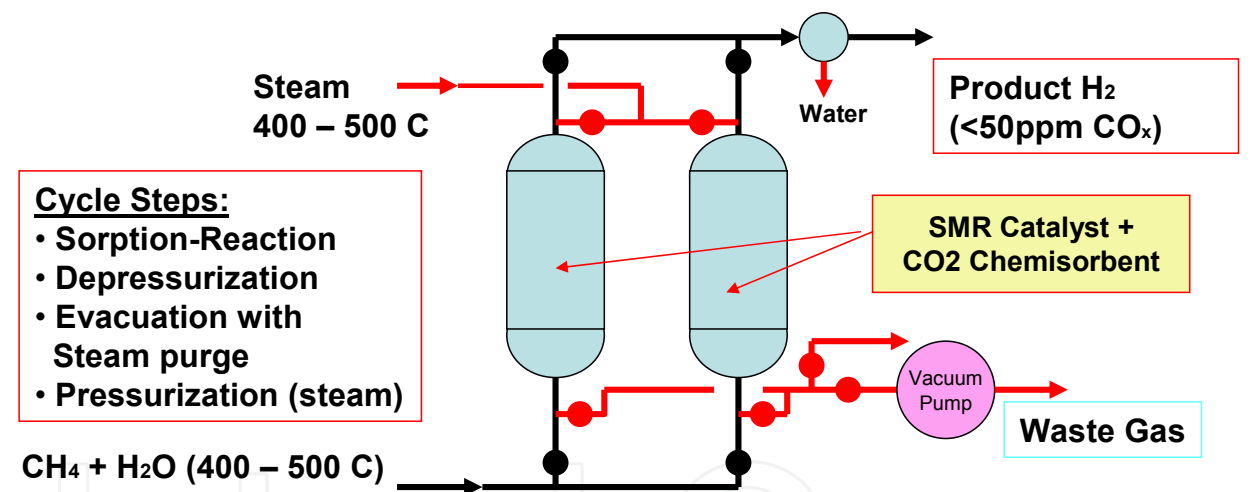

Fig. 15. Schematic flow sheet of a PSSER system.

Process	H_2 Product Purity (dry basis)	H_2 Productivity (mol/kg)	CH_4 to H_2 Conversion (net)	Steam Purge Duty (mol. steam per mol. of H_2 Product)
PSSER [Experimental] 6:1 H_2O:CH_4 Feed P = 1.78 bar; T = 490°C Catalyst = 33%	H_2 = 94.4 % CH_4 = 5.6 % CO = <30 ppm CO_2 = 40 ppm	0.25	73 %	7.5 (Needs Vacuum)
TSSER [Simulated] 4:1 H_2O: CH_4 Feed P = 1.5 bar; T = 490°C Catalyst = 10 %	H_2 = 99.99 % CH_4 = 60 ppm CO = 10 ppm CO_2 = 13 ppm	0.39	96.4 %	5.8

Table 3. Performance of PSSER and TSSER processes

Rodrigues and co-workers [46-50] developed a detailed mathematical model of the above-described PSSER process to simulate its performance for producing fuel-cell grade hydrogen. The model simulations were also used to investigate several new operational schemes for improving the performance of the PSSER process (higher conversion and purer H_2). They included (a) introduction of a purge step with a mixture of N_2 and H_2 prior to steam purge, and (b) packing different sections (three) of the sorber-reactor using different catalyst-sorbent ratios, the sections at the feed and the product ends being lean in sorbent, and operating the sections at different temperatures, the product -end section having a lower temperature.

Thermal swing sorption enhanced reaction (TSSER) process

A rapid thermal swing sorption enhanced reaction (TSSER) process for low temperature (~ 520 - 590°C) SMR was recently designed by Sircar and co-workers [51 - 53]. The process employed a pair of fixed bed sorber-reactors and it could directly produce fuel-cell grade H_2 using K_2CO_3 promoted hydrotalcite as the CO_2 chemisorbent in the process. The process uses two cyclic steps:

(a) **sorption-reaction step** where a mixture of H_2O and CH_4 is fed at a pressure of ~ 1.5-2.0 bar and a temperature of ~ 490°C into a fixed-bed reactor, which is packed with an admixture of the SMR catalyst and the chemisorbent, and which is pre-heated to ~ 520 - 590°C. The effluent from the reactor is fuel-cell grade H_2 at feed pressure.

(b) **thermal regeneration step** where the reactor is simultaneously depressurized to near-ambient pressure and counter-currently purged with superheated steam at ambient pressure and at ~ 520 – 590°C, followed by counter-current pressurization of the reactor with steam at ~520 – 590°C to the feed pressure. The reactor effluent for this step is a CO_2 rich waste gas.

The key advantages of the proposed TSSER concept over the above-described PSSER process are (a) elimination of the usually expensive, sub-atmospheric steam purge step for desorption of CO_2 and, consequently absence of a rotating machine (vacuum pump) in the process, (b) direct supply of the heat of endothermic SMR reaction from the sensible heat stored in the reactor at the start of step (a), (c) higher utilization of the specific CO_2 capacity of the chemisorbent in the cycle due to more stringent regeneration, (d) higher conversion of CH_4 to H_2, (e) higher purity of H_2 product, and (f) lower steam purge requirement per unit amount of H_2 product.

Figure 16 is a schematic drawing of a two-column embodiment of the concept using a shell and tube design of the sorber-reactors. The tubes will be packed with an admixture of the SMR catalyst and the CO_2 chemisorbent. The outside walls of the tubes will be maintained at a constant temperature by cross-flowing super-heated steam in the shell side. Figure 16 clearly exhibits the compactness of the proposed idea compared with the rather involved flow sheet for the conventional SMR-WGS-PSA route of Figure 7.
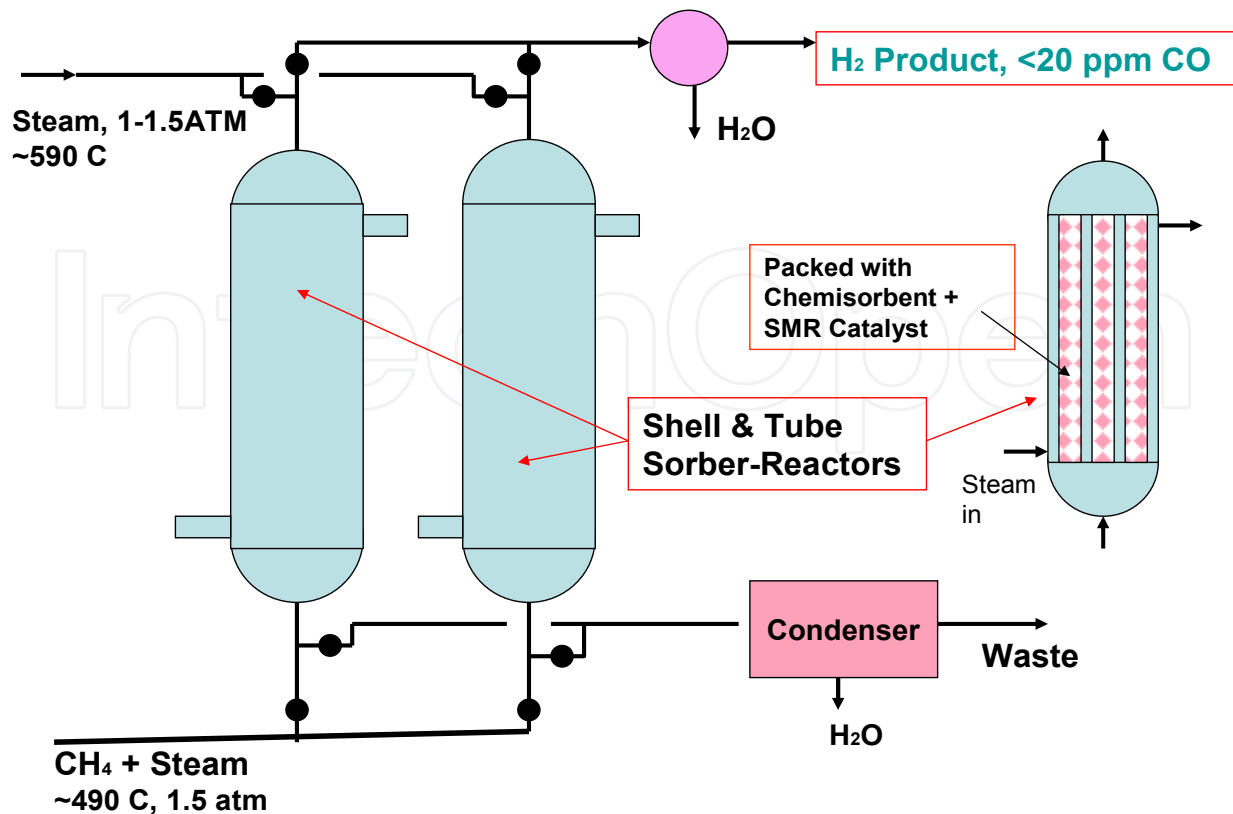
Steam, 1-1.5ATM ~590 C

H₂ Product, <20 ppm CO

H₂O

Packed with Chemisorbent + SMR Catalyst

Shell & Tube Sorber-Reactors

Steam in

Condenser

Waste

H₂O

CH₄ + Steam ~490 C, 1.5 atm

Fig. 16. Schematic drawing of the TSSER concept.

The performance of a TSSER process design [sorber-reactor tubes (I.D = 2.54 cm, length, L_c = 250 cm) packed with an admixture of a commercial SMR catalyst (10 %) and promoted hydrotalcite (90 %)] was estimated using a mathematical model which simulated the operation of the individual steps (10 minutes each) of the process. A detailed description of the model can be found elsewhere [51]. The thermodynamic and kinetic properties of the SMR reaction were obtained from the published literature [25, 54], and those for chemisorption of CO_2 are given by Figures 12 and 13. The feed gas ($H_2O:CH_4$ = 5:1, P = 1.5 atm. T = 450 C) was introduced to the sorber- reactor which was preheated to 520, 550, or 590 C.

Figure 17 shows an example of the simulation results. The profiles of CO_2 loadings are plotted as a function of dimensionless distance (L/L_c) in the sorber- reactor at the ends of steps (a) and (b) of the TSSER process at three different reaction temperatures [53]. The superior performance of the process at higher reaction temperatures is self evident.
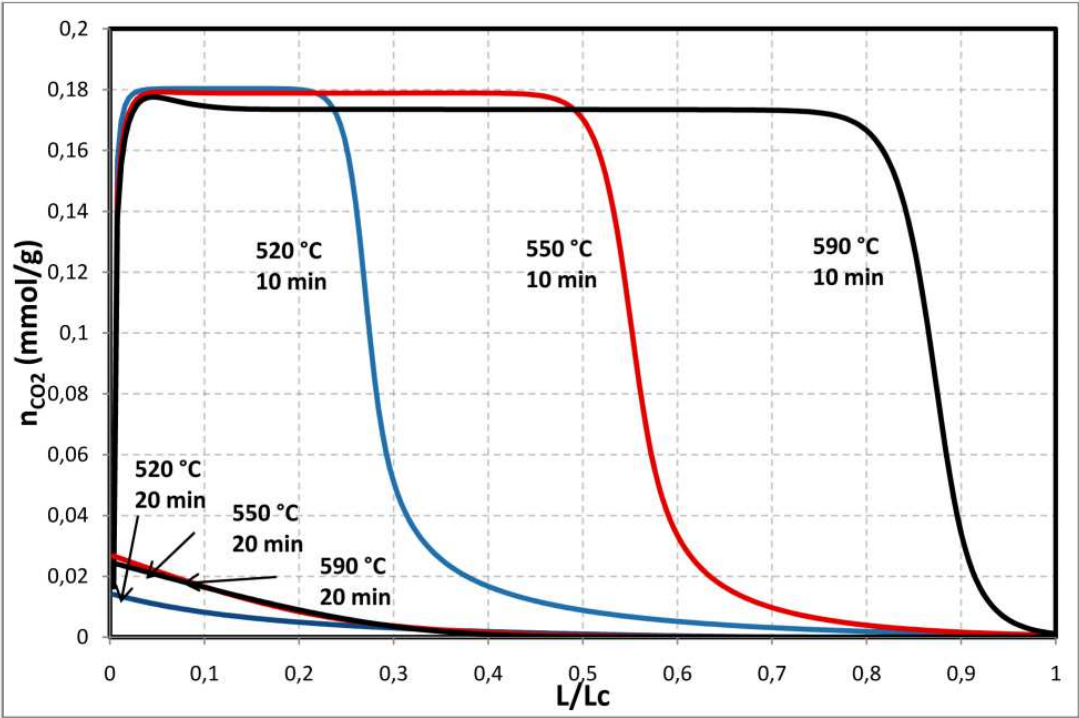
Fig. 17. Simulated profiles of CO_2 loadings in sorber-reactor: End of step (a) – solid lines (10 min); end of step (b) – dashed lines (20 min).

Table 4 summarizes the simulation results. It may be seen that the TSSER concept produces fuel cell grade H_2 by low temperature SMR with very high CH_4 to H_2 conversion at all temperatures. The specific H_2 productivity (mol. kg^{-1} of total solid in sorber reactor) however increases and the steam purge duty by the process decreases as the reaction T is increased from 520 to 590°C.

It may also be seen from Table 4 that the conversion of CH_4 to H_2 and the purity of H_2 product achieved by the TSSER concept far exceed those governed by the thermodynamics of catalyst-only SMR reaction (Figure 6 and Table 2) at any given temperature. Consequently, the concept permits operation of the SMR reaction at a much reduced temperature without sacrificing product H_2 conversion and purity.

Reactor Feed		Reactor T (°C)	H_2 Product Purity (ppm)	H_2 Productivity (moles/kg of total solid)	Feed CH_4 to Product H_2 Conversion (%)	Steam purge duty for regeneration in step (b) (moles/mole of H_2 product
CH_4: H_2O	Pressure (Bar)					
1:5	1.5	590	CO = 10 CO_2 = 13 CH_4 = 60	0.440	99.8%	7.2
1:5	1.5	550	CO = 10 CO_2 = 23 CH_4 = 129	0.296	99.5%	8.2
1:5	1.5	520	CO = 10 CO_2 = 31 CH_4 = 480	0.157	99.1%	13.3

Table 4. Simulated performances of the TSSER concept

The model was also used to evaluate the performance of the TSSER process under conditions identical to that used for the PSSER process reported in Table 3. The comparative results given in Table 3 demonstrate the superiority of the TSSER concept (higher H_2 purity, higher specific H_2 productivity by the catalyst-chemisorbent admixture, and higher CH_4 to H_2 conversion).

It should be mentioned here that the model was also used to simulate the performance of another rapid TSSER process designed for simultaneous production of fuel cell grade H_2 and a compressed CO_2 by-product stream to facilitate its sequestration from a synthesis gas produced by gasification of coal [55].

Thermal efficiency of the TSSER concept

A thermal efficiency for this process was defined as

$$\eta_{Th} = \frac{LHV_{H2\,Product}}{LHV_{NG\,feed} + LHV_{NG\,fuel}} \tag{4}$$

where $LHV_{NG\,feed}$ = heating value of the natural gas fed into the TSSER unit,
$LHV_{NG\,fuel}$ = heating value of supplemental fuel for (a) supplying additional heat of SMR reaction, (b) adding additional heat to feed and desorption gas streams, and (c) supplying heat of desorption to the bed for regeneration of the sorbent. Assuming LHV values of 120.1 MJ/kg and 47.1 MJ/kg for H_2 and natural gas, respectively, the thermal efficiency of the TSSER process was calculated to be 79.6%. This shows that the process is highly efficient for production of H_2 from CH_4.

The TSSER process will potentially provide an efficient but relatively simple and compact alternative for direct production of fuel-cell grade hydrogen by low temperature SMR without producing export steam.

Figure 18 is a heat integrated flow diagram of a TSSER concept designed for production of hydrogen for a 250 KW residential PEM fuel cell which requires ~ 3 kilo liters of H_2 per minute. The system contains two shell and tube sorber-reactors, heat exchangers, make-up heaters and blowers. Each sorber-reactor contains 2665 tubes [2.54 cm ID x 250 cm long, intra tube void fraction = 0.25, each packed with ~ 1.1 kg of an admixture of the SMR catalyst (10%) and CO_2 chemisorbent]. The feed (5:1 steam: methane) to the reactor was at 450°C and at a pressure of 1.5 bar. The reaction temperature was 590°C. The cycle time for each step was 10 minutes. The design was based on the simulated performance data of Table 4.
A first pass estimation of the capital and operating costs ($/kg of H_2) of the TSSER process for H_2 production for a 250 KW residential fuel cell is given in Table 5 which indicates that the cost is very competitive (cost of distributed production from natural gas ~ $ 2.5- 3.5 /kg of H_2)[56].

Design & Cost of a TSSER Process for a Residential Fuel Cell

Fig. 18. Tentative flow sheet for a TSSER system supplying H_2 to a 250 KW residential PEM fuel cell.

Capital Costs, $/kg H_2	250 kW
SER-SMR vessels	0.13
Over all Vessel dimensions	5.0' Dia. 8.2' High
Blowers	0.11
Heat Exchangers	0.02
Sorbent/catalyst	0.01
Total	0.27
Operating costs, ($/kg H_2)	
Electricity for blowers	0.65
Steam consumption	0.02
Supplemental heat	0.14
Total	0.71

Table 5. First pass cost estimation of TSSER process.

Summary

Decentralized residential power generation employing a H_2 PEM fuel cell requires that essentially CO_x free H_2 be produced on site by catalytic steam reforming of piped natural gas and then purifying the product H_2 (removal of bulk CO_2 and dilute CO impurities). Currently, it may be achieved by subjecting the reformed gas to water gas shift reaction followed by (a) removal of all impurities by a PSA process or (b) selective oxidation in a catalytic PROX reactor to reduce only the CO impurity below ~ 10 ppm for use in the fuel cell. The latter approach assumes that the detrimental effect of CO_2 on the performance of the fuel cell is minimum. This assumption may not be valid.

A recently developed thermal swing sorption enhanced reaction (TSSER) process scheme can be used to combine reformation, shifting, and purification in a compact, single unit operation for this application. The process permits circumvention of the thermodynamic limits of the SMR reaction and permits direct production of fuel cell grade H_2 with high recovery and purity, yet operating the SMR reaction at a lower temperature. Simulated performance of the process, preliminary process design for supplying H_2 to a 250 KW fuel cell, and first pass costs are described.

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