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Fuel processor – fuel cell integration: Systemic issues and challenges



Babita Kalmula, Vijaya Raghavan Kondapuram*

I.I.C.T., Hyderabad 500607, India

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ABSTRACT

Fuel processors (FPs) are integrated with fuel cells (FCs) for onsite and onboard power generation. The process technologies employed in FPs have to be properly selected on the basis of fuel characteristics, impurity tolerances and operating specifications of FCs. Chemical, thermal and process parameters need to be given due consideration to ensure smooth FP–FC integration. The chemistry and catalytic reaction engineering of H₂ generation in FPs and its utilization in FCs through electrocatalysis provide major challenges. The reactor configurations, extent of their miniaturization and their internal hydrodynamics and other design factors need to be considered for proper integration. This article highlights the current state of engineering knowledge in FP–FC integration and future prospects for achieving more efficient FP–FC systems for large scale onboard deployment.

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Abbreviations: AFC, Alkaline fuel cell; CO, Carbon monoxide; CO₂, Carbon dioxide; CPE, CO production efficiency; CPOX, Catalytic partial oxidation; ED, Energy density, kWh/dm³; EE, Energy efficiency; GHSV, Gas hourly space velocity; HPE, Hydrogen production efficiency; HTS, High temperature shift; IMP, Inlet manifold pressure; INEL, Idaho National Engineering Laboratory; LTS, Low temperature shift; MCFC, Molten carbonate fuel cell; OMP, Outlet manifold pressure; ORNL, Oakridge National Laboratory, USA; PAFC, Phosphoric acid fuel cell; PEFC, Proton exchange fuel cell; PEMFC, Proton exchange membrane fuel cell; PNNL, Pacific Northwest National Laboratory, USA; POX, Preferential oxidation; SE, Specific energy, kWh/kg

* Corresponding author. Tel./fax: +91 040 27193119.

E-mail address: kondapuramiict@yahoo.com (V.R. Kondapuram).

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1. Introduction

Though the fuel sources like methanol or natural gas can be used directly in fuel cells which are compact in nature, such systems have several drawbacks viz., lower power density and operational efficiency, slow oxidation kinetics of many hydrocarbon fuels and the need for extensive purification to remove undesirable impurities. The fuel cells incorporating separate fuel processors (FP) provide widest possible primary fuel options to generate hydrogen of required purity for the fuel cell (FC). The FP–FC integrated systems have accordingly gained higher acceptability levels. Also, the hurdles in developing an extensive hydrogen infrastructure for FCs have led to the incorporation of onboard reforming facilities in the form of FPs consisting of reformers, sulphur traps, water gas shift units and appropriate CO cleanup systems for generating hydrogen from a hydrocarbon source which are integrated with fuel cells (FC) for onsite power generation. Their operational efficiency depends on chemistry, thermodynamics, FP and FC system configurations, impurities and other factors. The FC component accounts for 33% of space and cost. The FPs along with power conditioners, air supply units, thermal management systems, water treatment facilities and process controllers account for the rest of the plant cost. The configuration of FPs depends on the type of fuel being used and the type of FCs to which they have to be integrated. They need to be customized for specific situations. The FP–FC integration poses major technological and engineering challenges. The published literature on this subject is rather scanty. This paper reviews the current status of FP and FC technologies, the major factors impacting their integration and future challenges to be overcome to make them more efficient and user friendly.

2. Basic features of FP and FC systems

2.1. FC classification and characteristic features

A FC is an electrochemical device that converts the chemical energy of a fuel like hydrogen directly into electrical energy. The FC technologies continue to attract research attention worldwide for developing novel distributed power stations, fuel cell vehicles and standby power units [1]. The FCs are classified according to the type of electrolytes employed in them as well as their operating temperature, fuel or oxidant used and cell design [2]. The important types are AFC, PEFC, PEMFC, PAFC, MCFC and SOFC. They are at various stages of commercial deployment based upon their applications and operating regimes. The AFCs, used predominantly in space missions, are expensive since they require pure H_2 and O_2 as reactants. PAFCs are preferred for distributed and centralized power production systems. They have achieved the widest commercial application. The PEFCs and PEMFCs which are the smallest and lightest of the designs are being employed in transport systems particularly for electrical vehicles. The recent developments on high temperature (100–200 °C) PEMFCs [3] have made it possible to achieve greater power efficiency and wider range of fuel usage in them. Their CO tolerance lies between 3000 and 5000 ppm with membrane durability of 20,000 h. They do not require humidified environment and are costed relatively less than, their low temperature counterparts. With increased fuel

flexibility and greater level of impurity tolerance, MCFCs and SOFCs which operate at hottest temperatures, are favoured for co generation or waste heat based power plants by taking advantage of the excess heat generated. Table 1 highlights FC characteristic features viz., operating temperatures, energy conversion efficiency, power application range, preferred application areas and desired impurity tolerances in hydrogen feed. Their materials of construction in determine their versatility or limitations in application [4]. Reaction engineering aspects of FCs will enable understanding of their nonlinear dynamic behaviour and mass and heat transfer problems [5]. The sensitivity of metal catalysts employed in them and their impurity tolerances have profound influence while evolving FP–FC integration strategies. They require ancillary facilities like manifolds, blowers, heat exchanges, humidifiers, condensers, valves and filters. Each application requires careful selection of hardware and software for achieving optimal performance.

2.2. FP chemistry and process technologies

FPs can utilize a variety of gaseous, liquid and solid fuels with H_2 as the common reductant. The rapidly increasing fuel costs and stringent GHG emission regulations have intensified the search for more eco-compatible fuel options [7]. Fig. 1 indicates the currently available lower carbon primary and secondary fuel options. The latter are employed as energy sources for FPs. The FP–FC systems employed for combined heat, hydrogen and power operates on hydrogen rich gases from anaerobic digestion of municipal waste water. Among the oxygenates, methanol (SE: 5.5 and ED: 4.4) is the most popular fuel for reforming since it requires mild process conditions and has the potential to attain highest conversion efficiency. Ethanol is gaining popularity for its ecofriendliness as well sustainability. Among the gases, natural gas (SE: 13.9 and ED: 2.3), propane and LPG are the most attractive fuels for FPs because of their large scale availability and high conversion efficiencies. Lee et al. [8] presented a compact and highly efficient natural gas FP consisting of a reformer and a water gas shift reactor. Eventhough, gasoline and diesel (SE: 12.6 and ED: 10.6) are attractive fuels due to their high specific energy density and easy availability, several S&T barriers have to be overcome for their deployment in FCs. Biomass (SE: 4.2 and ED: 3.0) and other solid fuels provide potential future options due to their carbon cycling neutrality and renewability. Synthetic liquid fuels from coal, biomass and natural gas are produced either by direct or indirect conversion process. Woody biomass can be pyrolysed to produce bio-oil which is deoxygenated to produce fuel suitable for FC application.

The Fuel processors have to be carefully designed to generate a relatively uniform hydrogen rich gas stream for a given FC [2,7,9,10] from the wide range of secondary fuels highlighted in Fig. 1. They contain widely varying classes of unwanted compounds that must be removed with different type of catalysts and associated post treatment processes. Some of the fuels are difficult to reform. Accordingly, a variety of reforming options have been reported (Fig. 2). Most widely employed process is steam reforming to produce synthesis gas with a high H_2/CO ratio. The auto thermal reforming option employs endothermic reforming along with exothermic oxidation reaction to provide a thermal balance. The steam reforming option requires more startup time than its

Table 1
Characteristic features and impurity tolerances of fuel cells.

Classification	Low temp.		Medium temp.		High temp.	
	PEMFC	AFC	PAFC	MCFC	SOFC	
1 Characteristic features						
1.1 Temperature range (°C)	40–80	65–220	205	650	600–1000	
1.2 Charge carrier	H ⁺	OH ⁻	H ⁺	CO ₃ ⁻	O ⁻	
1.3 Electrolyte	PE membrane/ perfluoro sulphonic acid	KOH	Phosphoric acid	Molten carbonate in LiAlO ₂	Yttria stabilized zirconia	
1.4 Catalyst	Pt	Pt	Pt	Ni	Inorganic or Steel	
1.5 Cell components	Carbon	Carbon	Graphite	Stainless steel	Ceramics	
1.6 Energy efficiency (%)						
Electrical	45 ⁺	60	40 ⁺	45 ⁺	38 ⁺	
Heat and power	70–90	> 80	> 85	> 80	90	
1.7 Power packs (kW)	1–250	10–100	50–1000	1–1000	1–3000	
1.8 Preferred applications	Backup power, automotive and small stationary platforms	Remote stationary power systems	Distributed power systems	Electrical, industrial and strategic areas	Residential and commercial	
2. Impurity tolerance levels						
2.1 CO	Poison (< 0.5%)	Fuel	Poison	Poison (< 10 ppm)	Fuel	
2.2 CO ₂	Diluent	Recirculated	Poison	Diluent	Diluent	
2.3 H ₂ O	Diluent	Diluent	Poison	Diluent	Diluent	
10 S	Poison	Poison	Poison	No studies to date (a)	Poison	
	< 20 ppm (H ₂ S)	< 10 ppm			< 1 ppm (H ₂ S)	
	< 50 ppm (COS)	< 0.5 ppm				
		(H ₂ S)				
11 NH ₃	< 0.2 mol%	< 1 vol%			< 5000 ppm	
12 Halogens	< 4 ppm	< 1 ppm			< 1 ppm	

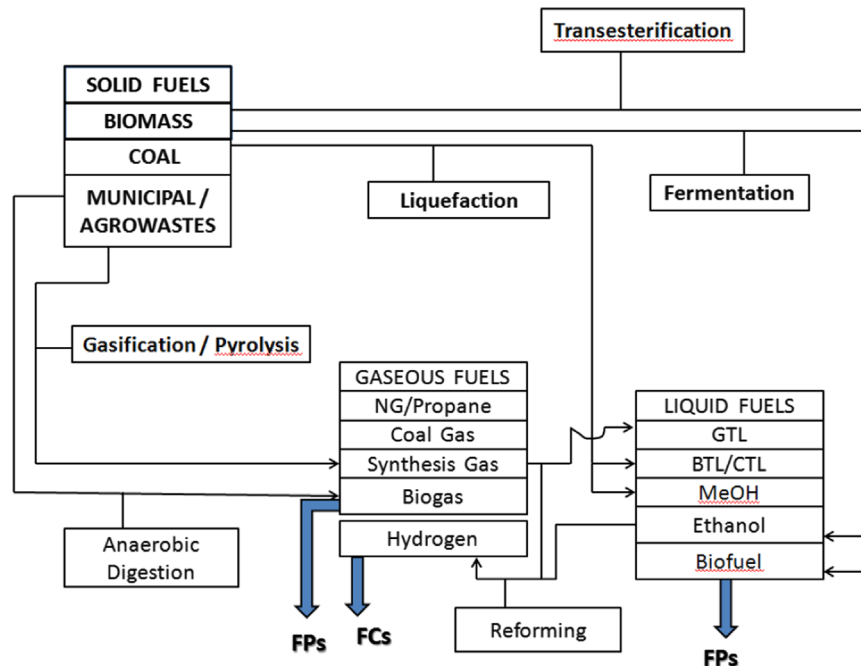


Fig. 1. Renewable and lower carbon primary and secondary fuel options for FPs.

autothermal counterpart. However, it provides H₂ concentrations above 75% as compared to 50% achieved by the autothermal option. The presence of catalyst poisons in the fuels add to the reforming process complexities and curtailment of their overall efficiency [6]. The sorbent enhanced reforming is an emerging technology for the production of high purity hydrogen from hydrocarbons with insitu CO₂ capture [11]. The ion transport

membrane reforming is an important platform technology proposed for natural gas as fuel. It combines air separation and partial oxidation or autothermal reforming in a membrane reactor [7]. Plasma reformers avoid the use of noble metal catalysts for gasoline or natural gas reforming. The core components are arc electrodes and a microwave nozzle for producing a stable arc torch [12]. Pressure swing reforming process has also been reported [13].

In actual practice the overall reaction scheme for reforming of hydrocarbon fuels to hydrogen comprises a combination of 4 other reactions coupled with reforming viz., catalytic partial oxidation, water gas shift reaction, preferential oxidation of CO and methanation. A compact FP system needs a combined reforming and insitu partial oxidation on the same catalyst bed to avoid any external heat source for the endothermic reforming process. Another pre-reforming operation that may be required for C_2 – C_6 hydrocarbons is hydrocracking to provide better reforming characteristics. Several technological options are thus available for small scale reformers for portable FP–FC systems. Ogden reviewed [10] their potential for integration with FCs.

The removal of CO from reformato to meet the allowable limits of FCs is one of the major challenges of FP–FC integration. Water gas shift reaction (WGSR) converts CO to form CO_2 and H_2 and is employed for CO removal from the reformates to the extent of 0.5–1%. It is a temperature sensitive reaction and is often employed as high ($350^+ \text{ }^\circ\text{C}$) and low (190 – $210 \text{ }^\circ\text{C}$) temperature options. Iron oxide promoted by chromium oxide and zinc/aluminium oxide catalysts are employed in HTS and LTS options respectively. Noble metal coated inorganic membranes are employed in WGSR for further improving hydrogen purity. A detailed review on this option is published recently [14] by the authors. The preferential oxidation technology enables CO oxidation on a heterogeneous catalyst to reduce it to 10 ppm level employing excess of oxygen (factor of 2). The instrumentation and process control strategies have to be worked out [15]. Catalytic CO methanation is another option for the purification of hydrogen rich gas mixture [16]. It is the reverse of steam methane reforming with no requirement of air. The CO concentration can be reduced from 0.5% to less than 20 ppm. The high temperature gasification/pyrolysis of solid fuels followed by the catalytic reforming of gas/liquid product is an emerging technological option for FPs [17]. Due to the difficulty in volatilizing the biomass based fuels, technologies based on aqueous phase reforming and supercritical water oxidation are receiving attention [18].

From engineering considerations, a FP systems consists of a three tubular reactors with each of them modelled as an isothermal plug flow reactor with minimal axial heat and mass transfer. The automotive onboard application places severe constraints on their volume. Kolavennu et al. [19] reported their design strategies.

2.3. FC and FP market opportunities

The fuel cell industry achieved its first commercial success in 2007 [20,21]. A significant growth in annual FC shipments worldwide has been reported since then. The global shipments were

80,000 units (63% stationery, 33% portable and 4% transport) in 2012 with more than threefold increase recorded in a single year. In megawatt terms, the installed capacity was 180 MW. This is due to a surge in the growth of combined heat and power units and portable consumer electronics chargers. The early market applications of material handling, backup power, residential CHPs and portable and auxiliary power packs have been achieved by 2011 [1]. However, fuel cell applications in transport sector continue to fluctuate on cost and compactness constraints inspite of their process technology successes. The PEMFC based UPS systems are now commercially available from 65 W to 400 kW range. 1 MW distributed stationary power systems based on PEMFCs have been commercialized in North America. 1 kW combined heat and power residential fuel cell systems based on LPG are undergoing field trials in Denmark. It is reported that 4–20 kW full find use in material handling and ground support equipments. Fuel cell power modules (75 W–150 kW) for hybrid buses are in use in North and South America and Western Europe. With reference to FPs, production of smaller reformer systems is an attractive mid-term option for integrated FP–FC systems for the automotive sectors in regions where low cost natural gas is readily available [7]. Steam, and autothermal reforming, partial oxidation and catalytic cracking of methane and ammonia for FPs are now receiving attention for large scale deployment. Multifuel FPs (suitable for 5 kW FCs) which can handle natural gas and a range of gaseous fuels have recently been field tested in Japan in residential sector.

3. FP–FC system integration

3.1. The major issues

The major challenge in FP–FC integration is to design a FP to precondition the H_2 rich gases adequately before they enter the FC stack. The complexities arise since feedstocks to FPs are endowed with incredibly variable composition and undesirable constituents. They have to be customized while integrating with FCs. In spite of the importance attached to the FP–FC integration, very few investigations have been reported on this subject. There is need to augment engineering knowledge in this area. The major issues impacting FP–FC integration are related to chemistry, thermodynamics, configuration and process control. Kolavennu et al. [19] reported an integrated model for a PEM fuel cell that utilizes methane as a fuel source. An overall energy analysis indicated the need for extra methane for meeting the endothermic heat requirement of the reforming process in FP. There are several other issues which need to be considered.

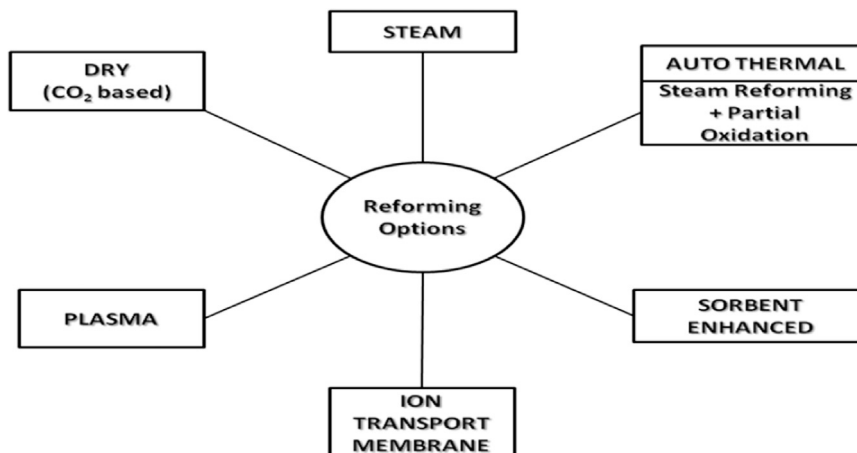


Fig. 2. Reforming options for FPs.

3.2. Impact of FP generated impurities on FC performance

Impurities present in the primary fuel and/or generated during the reforming and other processes can adversely impact the FC performance. The air input to FCs may contain NO_x and SO_2 . Table 1 provides the tolerance limits of CO, CO_2 , H_2O , S, NH_3 and halogens to be present in hydrogen feed to a FC. CO is unacceptable to PEFC, PEMFC, PAFC and MCFC systems since it can poison their Pt and Ni catalysts by tightly binding to them and preventing them from accessing hydrogen. As little as 10 ppm CO in reformat from a FP can poison the platinum catalyst of a fuel cell. Attempts have been reported [2] to enhance the CO tolerance limits of PEMFCs to 500 ppm level. They employed 0.5% air bleed to the anode with an optimized membrane electrode assembly. Efforts are also being made (a) to develop a Pt–Ru catalyst which can block CO absorptions and (b) to employ tungsten catalyst enriched with titanium dioxide nanoparticles [22]. Li [23] modelled CO poisoning and O_2 bleeding in a PEMFC. The model considered H_2 , CO and O_2 absorption, desorption, electro oxidation and heterogeneous oxidation kinetics. The effect of O_2 and air bleeding on CO poisoning was simulated with appropriate experimental validation. CO_2 acts as a diluent in almost all FCs, it is considered as a poison in PEFC and PEMFC. It undergoes reverse water gas reaction with the hydrogen adsorbed on the catalyst. It makes a large part of catalyst surface area inactive for H_2 dissociation. Jansen et al. [24] employed cyclic voltammetry and chromocoulometry to study the CO_2 poisoning in a PEMFC.

The sulphur containing impurities can severely degrade the performance of all FCs. Uribe, Garzon et al. [25,26] evaluated the effects of H_2S and SO_2 on PEMFCs. They found the degrading effects are very severe as well as irreversible due to catalyst poisoning. Fuel desulphurization is a prerequisite to overcome sulphur poisoning effects. The other impurities are halogens, NH_3 and NO_x . The presence of NaCl may contaminate the cathode air supply in FCs and decrease their protonic conductivity as a consequence of H^+ exchange with Na^+ at the catalyst layer. Ammonia decreases both the onset potential and current of the oxygen reduction reaction in FCs. Water treatment is the predominant removal mechanism for ammonia poisoning. NO_x adversely affects the membrane resistance in PEMFC possibly due to ammonium ion formation due to NO reduction by hydrogen.

4. The challenges of FP–FC integration

4.1. FP chemistry and engineering

Hydrocarbons or their derivatives can be represented by $\text{C}_n\text{H}_m\text{O}_z$ for evaluating the product distribution in reforming. Based on the specific energy and density characteristics of gaseous, liquid and solid fuels, the volume of generated hydrogen can be evaluated. The diesel oil has the highest energy density as compared to all other fuels. It has more non-volatile components than gasoline in 160–370 °C temperature range. As discussed in Section 2.3, the FP converts a primary fuel into hydrogen rich gases and then follows up with a number of processes to remove its undesirable constituents for onboard application. The FC electrochemistry is prone to poisoning by impurities present in hydrogen rich gases from FP. Table 2 highlights the chemistry and broad process conditions applicable to FP and FC reactions. Most of the reactions are catalytic and are either endothermic or mildly exothermic in nature.

Recently, Schmitt et al. [27] made an excellent review of fuel process technologies from fuel cell application perspective. Fig. 3 shows the most preferred fuel process options for various

categories of fuel cells. They are dictated by the post reforming purifications to meet the FC input specifications and logical unit processes and operation to achieve them. Gasification technologies produce varying levels of organic tars and particulate matter. The former cause coke formation on catalysts or on FC electrodes leading to their deactivation. Extensive purification is required in making them suitable for FC application. Sulphur needs to be removed from the gaseous or vaporized liquid fuel for direct use in high temperature fuel cells like SOFC and MCFC. The desulphurized gas/vapour is mixed with atmospheric air for partial oxidation or mixed with steam for steam reforming. The water gas shift reaction can be employed to remove most of CO in hydrogen rich gas mixture prior to its feeding to medium temperature fuel cells like AFC, HT–PEMFC and PAFC. It can be further purified with preferential oxidation to remove CO to less than 10 ppm level for use in PEMFC. In order to prevent H_2 starvation catalytic burning is employed to generate thermal energy from excess hydrogen exited from the FCs.

Reaction engineering of FP processes are important for designing the reactors to provide desired H_2 output. The reforming reactions are mainly controlled by the external mass transport from bulk to the catalyst surface as compared to intra-particle diffusion inside the catalyst pores. High GHSV in the catalyst bed is maintained to minimize the external mass transfer resistances. Kamp et al. [28] reported the space velocities of 200,000 h^{-1} for reformer, 60,000 h^{-1} for WGS and 150,000 h^{-1} for CO removal by oxidation, respectively. This is in contrast to GHSV of 1000–3000 h^{-1} maintained in industrial hydrogen plants.

The method of introducing the reactants in the FP process train, influences the mass transfer and kinetic processes [4]. The catalyzed reactions in FP units may be far from optimized from reaction engineering considerations. With their catalyst effectiveness factor at less than 0.5. Their mechanisms are not that well understood to evolve a failproof strategy to achieve higher process efficiency. The use of engineered catalysts is attaining importance [29,30] to achieve highest power density and specific power of integrated FP–FC limits. Autothermal reactors combine the thermal effects of CPOX and SR reactions by feeding the fuel, water and air together into the reactor. Kinetically the two processes occur simultaneously in the presence of a catalyst and their rates need to be balanced to achieve the required thermal balance. In an interesting study, Authayanum et al. [31] analysed the effects of different fuel processors on HT and LT–PEMFC systems with reference to CO concentration the H_2 feed. They concluded that the HT–PEMFC has shown the highest system efficiency when WGS reactor is introduced in the FP circuit.

4.2. FC chemistry and engineering

A FC consists of a positively charged cathode and a negatively charged anode, an electrolyte and an external load (Fig. 4). The anode provides the necessary interface between the fuel and the electrolyte, catalyses the fuel transformation to hydrogen and provides the pathway for free electrons to move to the external circuit. Simultaneously the cathode provides an interface between the oxygen and the electrolyte, catalyses the oxygen reaction and provides the pathway for free electrons to the oxygen electrode via the external circuit. The electrolyte acts as H_2 – O_2 separator and completes the electrical circuit of transporting ions between the electrodes. A typical fuel cell operates at 0.55–0.8 V with the theoretical maximum being 1.48 V. Since the electrical current is the product of operating voltage and current, certain amount of heat is generated in the fuel cell. The heat is carried by the water produced in the FC as water vapour. Table 2 highlights the electrochemical reactions associated with the four major types of fuel cells at their anodes and the cathodes. At the anode, hydrogen

Table 2
The reaction chemistry of fuel processors and fuel cells.

			Type	Temp (°C)	Catalyst
1	FP reactions				
1.1	Hydro desulphurization of CH ₄	$RSH + H_2 \rightarrow RH + H_2S$	Mild exo	300–400	RuS ₂ , MOS ₂
1.2.	Partial oxidation (catalytic)	$C_nH_m + \frac{m}{2}O_2 \rightarrow nCO + \frac{m}{2}H_2$	Exo	800–900	Ni, Rh, Pt, Ru
1.3	Steam reforming	$C_nH_mO_2 + y(O_2 + 3.76N_2) + 2(n - Y - \frac{m}{2})H_2O$ $\Leftrightarrow nCO_2 + 2\left(n - y - \frac{Z}{2} + \frac{m}{y}\right)H_2 + 3.76y N_2$	Endo	700–850	Ni/Al ₂ O ₃ , Rh, Ru
1.4	Oxidative steam reforming	$C_nH_m + nH_2O \Leftrightarrow nCO + (n + \frac{m}{2})H_2$	Neutral	160–300	La/Ca/Fe oxides
1.5	Water gas shift reaction	$CO + H_2O \Leftrightarrow CO_2 + H_2$	Mild exo	180–260	Cu/Xn/Al ₂ O ₃
1.6	Preferential oxidation	$2CO + O_2 \rightarrow 2CO_2$	Exo	80–180	Pt, Ru, Au, CuO
1.7	CO methanation	$CO + 3H_2 \Leftrightarrow CH_4 + H_2O$ $CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O$	Exo	240–280	Ni/zrO ₂ Ru/TiO ₂
1.8	Catalytic H ₂ combustion	$3H_2 + O_2 \rightarrow 2H_2O + H$ $2H + M \rightarrow H_2 + M$	Exo	400–450	Pt
2	FC reactions				
2.1	PEMFC				
2.2	Hydrogen proton formation	$2H_2 \rightarrow 4H^+ + 4e^-$	Anode	60–120 °C	Pt
	Water formation	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ Overall $H_2 + 1/2 O_2 \rightarrow H_2O$	Cathode Exo		
	AFC				
2.3	Water formation (at anode)	$H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$	Anode	190–200 °C	Ni
2.4	Hydroxyl ion formation	$1/2O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$	Cathode		
	SOFC				
2.5	Water and CO ₂ formation (at anode)	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ $CO + O^{2-} \rightarrow CO_2 + 2e^-$	Anode -do-	600–1000 °C	Ni cermet
2.6	Hydroxyl and oxygen ions formation (at cathode)	$CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e^-$ $1/2 O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$ $1/2 O_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	-do- Cathode -do-		
	MCFC				
2.7	Water formation	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	Anode	~650 °C	Ni
2.8	Carbonate ion formation	$CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^-$ $1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	-do- Cathode		

* Applicable for oxidative steam reforming.

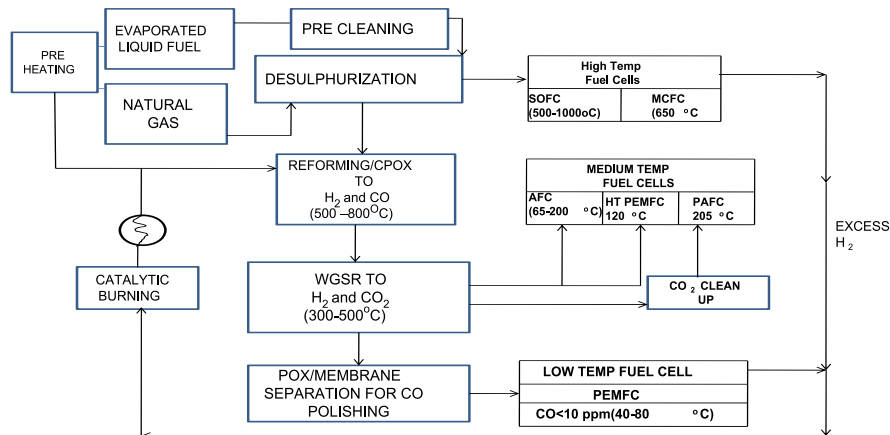


Fig. 3. Fuel processing requirements for various fuel cells.

gas is electrochemically dissociated into H⁺ and free electrons and at the cathode, oxygen gas is electrochemically combined in the presence of a catalyst with hydrogen ions and free electrons to form water. The overall water formation reaction energy is equal to the Gibbs free energy difference between the product and the reactants.

Under typical operating conditions, the anode utilizes around 80% of the hydrogen provided by the fuel processor. As a result, the flow existing at the anode is still rich in hydrogen. Leaving it in fuel cell exhaust not only compromises the hydrogen utilization efficiency but also lead to thermal and environmental problems. Introduction of a catalytic hydrogen burner will enable recuperation of this material loss and convert it to thermal energy. It can be used to preheat the fuel and

air to FP thus reducing its dependence on external sensible heat source. Sourapas et al. [32] developed a dynamic model of FP–PEMFC system with a catalytic burner to understand hydrogen starvation phenomenon during current load transients. They also studied the current load decrease when hydrogen utilization at the anode drops suddenly. The water generated at the cathode has to be expeditiously removed as water vapour to provide better O₂ access to the cathode. It can also be achieved by the alteration of the humidification levels of the reactant gases. A remarkable analogy exists in the water balance in FCs and energy balance in an exothermic chemical reactor as evidenced by the studies of Chia et al. [33].

The chemical integration problems within FCs are not as many as those in FPs. The reduction in cell voltage is one of the time

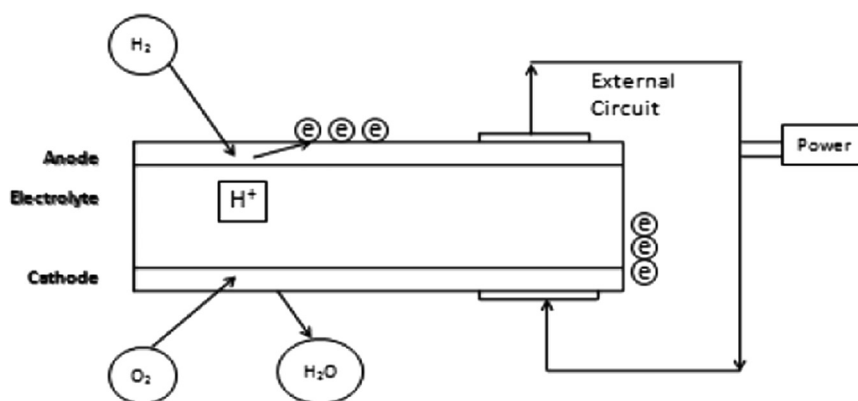


Fig. 4. The electrochemical process and current circuit in a fuel cell.

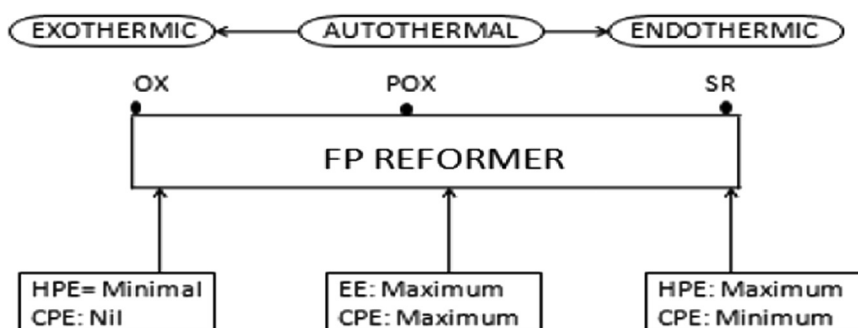


Fig. 5. Optimal energy vs. H_2 production efficiency.

variant factors. It occurs due to activation losses, fuel cross over, internal currents and ohmic and concentration losses. The cathode reaction is 100 times slower than that of the reaction at the anode and it can limit the power density of the cell. The fuel cross over occurs from anode to cathode without releasing electrons through the external circuit. It decreases the cell efficiency. The concentration losses occur due to reduction to H_2 and O_2 at the electrodes due to build up of water at the cathode.

5. Overall thermal performance of FP–FC systems

5.1. Thermal analysis

The energy efficiency of an integrated FP–FC system depends on its individual unit configurations, the composition of hydrogen feed to FC and the operating conditions. The thermal management opportunities in FCs were reviewed by Faghri and Guo [34]. The thermal balancing of a FP–FC system is important for ensuring high material and thermal efficiencies and rapid dynamic response of the system. Regulated thermal energy input to a FP. It will (a) provide the proper trigger for the introduction of rate controlling reactants viz., oxygen and water (b) ensure optimal operating temperatures in the catalyst beds and (c) keep the temperature of exhaust gases and external surfaces of the reactors within the allowable limits. The thermochemical efficiencies of FP reformers provide vital clues on their operating domains (Fig. 5) shows the maximum hydrogen production efficiency (HPE) occurs under steam reforming conditions while it is minimum under total oxidation conditions. As the operation moves from steam reforming to oxidation, the carbon monoxide content increases and reaches a maximum under partial oxidation conditions. The local minima of CO occurs under the steam reforming conditions.

However, from the standpoint of energy efficiency, its maxima occurs under an autothermal condition since it represents thermal neutrality

Thermodynamically, the constraints imposed by selectivity or a desirable product distribution in any chemical reaction dictates the Gibbs minimum energy and the thermodynamic equilibrium compositions. The activation energy barriers separate the products from reactants in FPs and FCs. Semelsberger et al. [35] employed the Gibbs free energy minimization approach for generating hydrogen rich FC feeds from dimethyl ether steam reforming. He found that the maximum hydrogen production efficiency of 97% occurs at a steam to carbon ratio of 1.5, a temperature of 200 °C and a pressure of 1 atm. He later identified the thermodynamically stable products. In the context of FP–FC integration, the effect of steam dilution is found to be important as the steam to carbon ratio is increased beyond 2.5. He also studied the thermodynamics of hydrogen production from the combined processes of dimethyl ether steam reforming and its partial oxidation. The product water produced at elevated temperature in FCs carries thermal energy which cannot be converted into electricity without employing a steam turbine. This has led to the development of hybrid FC–turbine combine cycle systems to attain an electrical efficiency in excess of 70%.

An exergy analysis provides the overall thermodynamic efficiency of a FP–FC system. It is based on the second law of thermodynamics and the concept of irreversible production of entropy. It can indicate the conditions for improvement of reforming, oxidation and other processes in FPs. Significant work in this area has been done in PNNL, INEL, ORNL and some universities in USA [36]. Delsman et al. [37] employed exergy analysis for evaluating methanol, ethanol, octane, ammonia and methane as primary fuels. In the case of methanol processor integrated with PEMFC, it was shown that the largest exergy loss occurs in FC,

burner, vaporizer and reformer. The overall exergetic efficiency of the system was found to be 37%. Chan et al. [38] made the exergy analysis of a SOFC based power system to show that the water vaporizer, burner and reformer units lead to higher exergy destruction.

6. Design approach and system analysis

6.1. Design strategy

The efficiency and ease of operation of an integrated FP–FC system greatly depends on the reactor configurations selected for FP and FC units and the extent of chemical and thermal integrations achieved. Qi [4] reviewed the major reactor configurations employed for FPs. They include annular, cylindrical, plate assembly and micro-channel type configurations. The annular configuration (Fig. 6) integrates the desulfurization, steam reforming, WGS, CPOX and allied heat exchanges in a single unit and can achieve high reaction efficiencies by making optimal use of waste process streams. The cylindrical FPs are radial reactors with various reaction zones placed sequentially in space adjacent to each other within the process space. They have lower pressure drops and better temperature control. A packed plate assembly type configuration makes it easier for scale up. The reformer and combustor units can be located at adjacent spaces to share a common wall between them. Compared to the conventional reformers, the scale up problems are minimal with this configuration. The microchannel configuration integrates a micro-reactor with a microchannel heat exchanger. An efficient fuel injector with ability to completely mix the liquid fuel with high temperature steam will minimize coke formation on the catalyst particles/coating. Recently direct droplet impingement reactor was employed for liquid hydrocarbon fuel for miniaturized FP–FC system [39]. It can be coupled to CO/H₂ active membrane piston facility for precise control of reactor volume. Plate type configuration consisting of an assembly of flow (or separator), sealing, electrolyte and electrode plates. Flow plates connect two adjacent cells to control flow patterns and to ensure even distribution of liquid/gaseous feed across the cell area. On the back side of the stack, cooling/heating liquid is provided to the heat exchangers. Apart from repeating units, a stack contains two end plates and two electric current collector plates. Ilhan et al. [40] reported for an integrated NG based FP–PEMFC system and the importance of FP design.

6.2. System analysis through simulations

In order to get a complete idea on the effect of system configuration and operating parameters on integrated FP–FC

system efficiency, a comprehensive analysis of different configurations need to be undertaken. Each option has to be investigated by varying the most critical operating parameters. The system analysis consists of thermodynamic and transport modelling. It will allow identification of the most promising FP–FC configuration in terms of energy efficiency and the hydrodynamic features of the contactors. ASPEN [41] reported software packages R GIBBS & R STOIC for analysis of FP–FC systems to assist in drawing flowsheet of reformer, CO clean up systems and a fuel cell along with reactant and product compositions. Simulations are performed under steady state conditions in FP and chemical and phase equilibrium data is generated by employing Gibbs energy minimization concept. In the case of FC, the anode is modelled as an ideal separator and the cathode as an isothermic reactor. Menna et al. [42] performed the first level of system analysis using the above software packages for conventional and membrane based FP–FC systems with various process options to estimate the overall energy efficiency. For similar configurations, a simulation study was performed using a heterogeneous transport model for packed bed reactors. The cost structures of integrated FP–FC systems were analysed by James et al. [43] at various production rates.

6.3. Miniaturization of FP–FC systems

Major design, fabrication and processing challenges occur in the development of portable integrated FP–FC systems for automotive sector. Hydrogen production from miniaturized fuel processors require innovative options for depositing catalysts onto metallic microstructured platelets for reforming and water gas shift reaction stages. The design of miniaturized FPs and FCs require steady state and dynamic reactor modelling (CFD), proper sizing of sensors and actuators, gas/liquid feeding systems, catalytic burners and electrolytic cells. During their fabrication, advanced micromachining techniques, state of art deposition techniques for catalysts on microstructured platelets and a series of Co and countercurrent heat exchangers have to be employed. Elmer and Riffat [44] made a state of art review of fuel cell micro CHPs in the residential building sector.

6.4. Performance modelling

The steady state and transient models are employed for assessing the performance of FP–FC integrated systems along with the auxiliary units (Fig. 7). Two major reviews have been published on this subject [45,46] with focus on integration issues. Table 3 highlights the type of models employed for simulation processes. Steady state models are typically used for component sizing, trade off analysis and fuel performance evaluation. They need to be

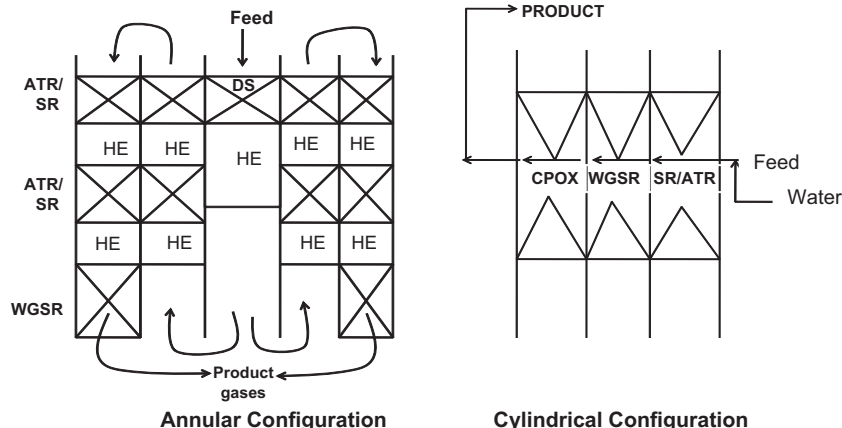


Fig. 6. Annular and cylindrical reformer configurations.

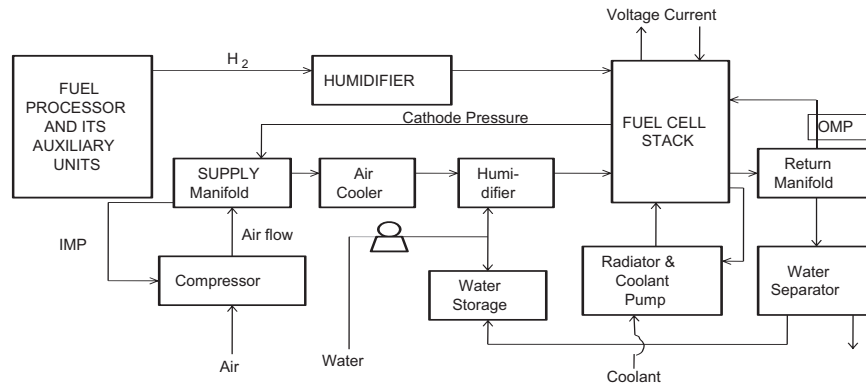


Fig. 7. A typical equipment hook up in a FP–FC integrated system.

Table 3

Modeling of FP–FC systems and application in PEMFC.

No Modeling approaches		Model applications in FP–PEMFC system		
FP–FC component	Model physics	Focus	Study outcome	Reference
1 FP (Reformer, CPOX, WGSR and others)	Pseudo-homogeneous transport in packed beds	Energy efficiency	Fuel performance and process efficiency	[34]
2 Compressor	Airflow mapping, thermo-dynamic computations and motor inertia	Heat and power systems	Energy recovery as rate limiting step and water balance	[36]
3 Manifolds	Mass and energy conservation/balances; dynamics	Configurations	Effect on system efficiency	[35,37]
4 Air cooler	Thermal change and humidity	Membrane separation	Feed requirements and additional power	[35,38]
5 Humidifier	Mass transfer in humidification	System analysis with ASPEN PLUS	Performance of SR VS ATR	[35,39]
6 FC stack	Stack voltage, anode and cathode flows and membrane hydration			

evolved for each unit present in FP–FC system with defined operational boundaries. Dynamic models are used for assessing the temperature transients in the FP–FC systems. Pasdag et al. [46] employed condensing burner technology for maximizing the electrical efficiency of steam reforming FP–PEMFC system. Salemmme [47] showed that membrane facilitated FP increases the integrated system efficiency from 48% to 52%. Ivanov et al. employed flat ultra thin membrane of palladium alloy [48]. For airborne power generation, a microstructured FP based on partial dehydrogenation of kerosene was employed successfully [49]. Seo et al. [50] employed dual pipe geometry for natural gas based FP integrated with PEMFC for residential buildings. Lee et al. [8] integrated a natural gas reformer coupled with a water gas shift converted with a 1 kW PEMFC for residential applications. An autothermally reformed and gas fuelled PEMFC has been analysed by Doss et al. [51] for FP and integrated system performance including its thermal integration aspects. Yoon et al. [52] studied the diesel based FP–SOFC system. Borup et al. [53] analysed the fuel effects on FP durability and carbon formation for automotive applications. Song [54] examined the competitiveness of different fuel options for an integrated FP–PC system.

7. Control strategies for integrated FP–FC systems

Accurate control of FP outflows minimize the deviations in H_2 concentration at the FC anode as well as large temperature excursions in the FP downstream process units. For example, good regulation of CPOX temperature will ensure accurate regulation of anode hydrogen concentration and prevents the fuel stack from hydrogen starvation. The control strategy for a FP–FC integrated

system is basically to protect the FP stack from damage due to H_2 conversion in FP train. It is quite complex on account of intra system interactions and their conflicting control logics. Gorgun et al. [55] evolved feedback controls for CPOX, WGSR and POX reactors in a FP–FC power system. Pukrushpan et al. [45] studied partial oxidation in natural gas based FP–FC system to regulate both CPOX temperature and anode hydrogen concentration. Chen et al. [56] evolved startup strategies for a FP consisting of a reformer, WGSR and POX reactors linked to a PEMFC. They formulated the startup as a constrained optimization problem which is amenable to numerical solution. In a very recent study, Basuldo et al. [57] developed modelling, simulation, fault diagnosis and advanced controls for FP–PEMFC with bio ethanol as feed.

8. Summary

The integration of FP–FC systems pose major challenges due to technical factors including variable fuel compositions and their undesirable impurities and problems related to process chemistry and thermal, configuration and process complexities. This review paper has highlighted the important integration issues with the help of reported case studies. It has shown that more concerted efforts are needed to effectively integrate a variety of FP and FC process units for a host of stationary and mobile applications. A multidisciplinary approach utilizing the advanced knowledge base of organic and electrochemistry, applied catalysis, thermodynamics, chemical reactor design engineering, modelling and simulation, process control and dynamics is required to address vital aspects of the FP–FC integration effectively.

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