Renewable and Sustainable Energy Reviews 60 (2016) 450–463

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Solid oxide fuel cell operating with biomass derived producer gas: Status and challenges

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ARTICLE INFO

Article history:
Received 25 June 2015
Received in revised form
26 December 2015
Accepted 13 January 2016

Keywords:
Biomass gasification
Producer gas
SOFC
Tar
Carbon deposition
Contaminants
Cermet

ABSTRACT

Solid oxide fuel cell as a conversion device is finding importance in the energy sector due to its high efficiency, low emissions and fuel flexibility. The use of producer gas as a fuel is gaining importance due to certain advantages over the conventional fuels while challenges lie in its usage due to the inherent contaminants present. This paper consolidates the efforts carried out using fossil fuels and highlights the challenges, and further, the progress made in the use of producer gas is critically examined. The effects of contaminants such as tar, particulate matter, H_2S etc. on anode materials are highlighted, and the published results are consolidated to examine whether the maximum tolerance limits of the contaminants be identified. However, it is observed that due to many inexorable factors viz., differences in the electrode material, microstructure, diverse operating conditions, the conclusions obtained are diverse and it is difficult to predict the general behavior of a particular contaminant. The need for a comprehensive study having both experimental and theoretical components focusing on the role of contaminants under the same operating conditions and using the same materials is highlighted as a major conclusion of this study.

Contents

1. Introduction

Rising energy consumptions and higher emissions from combustion devices operating with conventional fuels demand

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http://dx.doi.org/10.1016/j.rser.2016.01.075
1364-0321/

alternate energy sources, and Solid oxide fuel cell (SOFC) being an efficient, environment friendly, fuel flexible energy conversion technology is able to attract the attention of researchers [1]. Over the last two decades, significant progress has been made on SOFC, especially on the materials to support high temperature operations and different fuels [2]. However, commercialization of the technology is hindered by a few important factors, and the production and storage of hydrogen (H_2) which is being considered as an ideal fuel are major challenges [3]. As an alternative, the use of renewable fuels is desirable, and producer gas (PG)/syngas generated from biomass has received widespread attention due to its carbon neutrality nature [4].

Biomass generates both liquid and gaseous fuels; however the conversion efficiency of biomass to liquid is low (Fig. 1) [5], and this makes the use of gaseous fuel more prevalent. IC engine is the most common route due to the simple design and lower capital cost. Significant efforts have gone on using diesel engine on dual fuel mode [6–8] and gas engines on PG alone mode [9–12]. It must be emphasized that significant research towards operating the engine with PG has been carried out and the required gas quality for engine application has been established. Attempts have also been made in the use of gasifier for micro-gas turbine (mGT) applications [13]. However, recent attention is focused on fuel cell (FC) for it being more efficient than IC engines, and SOFC receives significant attention (Fig. 2) [14].

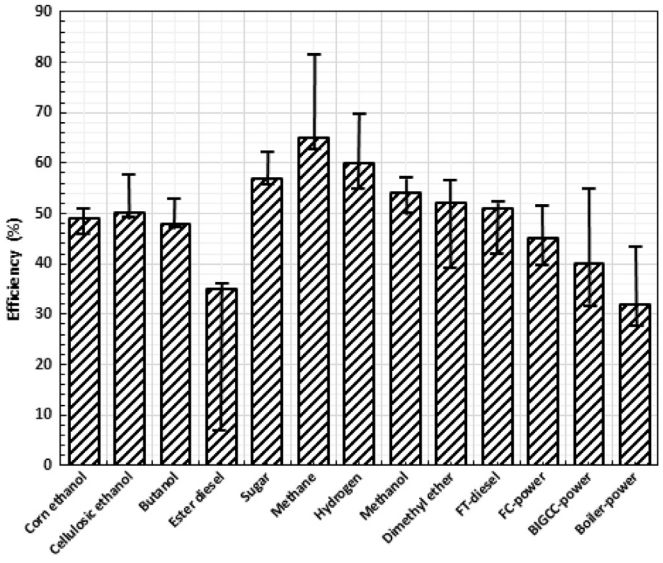

Fig. 1. Comparison of biomass to fuel efficiency in the bio-refineries or power stations [5].

Coupling of FC with a gasifier is a recent concept, and various research groups have investigated the possible trouble in handling the contaminants: tar, H_2S, HCl, etc., of the gases, and their short-term impact on cell components has been reported. However, the existing literature does not provide a future roadmap; since the results obtained are diverse due to differences in methods, materials and operating conditions. Use of SOFC with PG as a fuel is not well documented although there are many review reports wherein the SOFC is discussed in general or from the materials point of view. This paper attempts to consolidate the experimental and numerical studies reported in the literature towards arriving at specifications of PG for SOFC, based on the current experience available. Challenges and issues addressed in the choice of material and its behavior under various operating conditions are also reported.

The paper is structured as follows. First, a background on the need for SOFC is discussed followed by a brief introduction to the producer gas fueled SOFC in Section 2. Section 3 summarizes the progress in the materials development. Section 4 highlights the aspects of biomass gasification and the performance of the systems for power generation and Section 5 focusing on the experience in using biomass gasification for SOFC and presents the status of the technological advancements. Section 6 provides the conclusions with respect to the use of gasifiers for SOFC applications and highlights the challenges and possible roadmap.

2. Solid oxide fuel cell with PG: electrochemical reactions

SOFC working with PG can utilize three different fuels viz., H_2, carbon monoxide (CO) and methane (CH_4), unlike PEMFC working with H_2, and the literature on general view of FC and its working principle is largely available in many textbooks and reports [2,14–22]. In the use of PG as fuel, the additional anode side reactions (equations (3) and (4)) need to be considered. Fig. 3 illustrates the working of the producer gas fueled solid oxide fuel cell.

Cathode side: $O_2 + 4e^- \rightarrow 2O^{2-}$ (1)

Anode side: $2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$ (2)

Anode side: $CO + O^{2-} \rightarrow CO_2 + 2e^-$ (3)

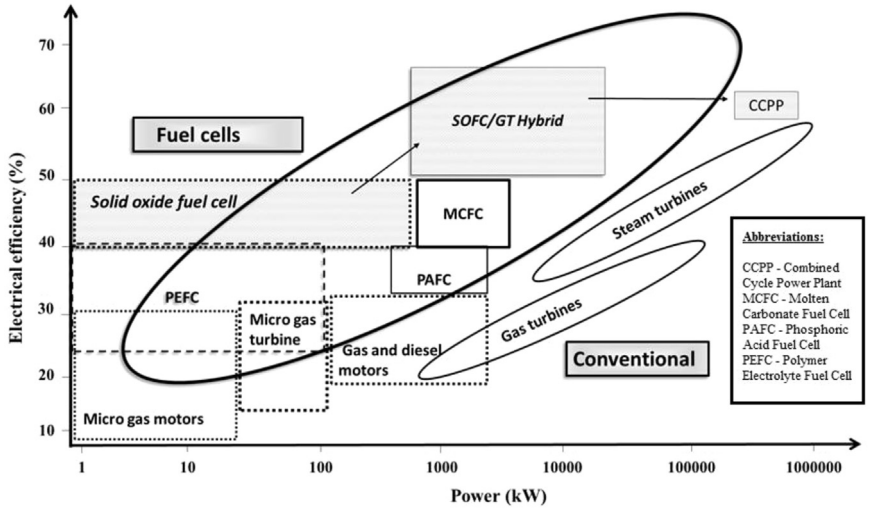

Fig. 2. Efficiency potential of various power generation technologies [14].

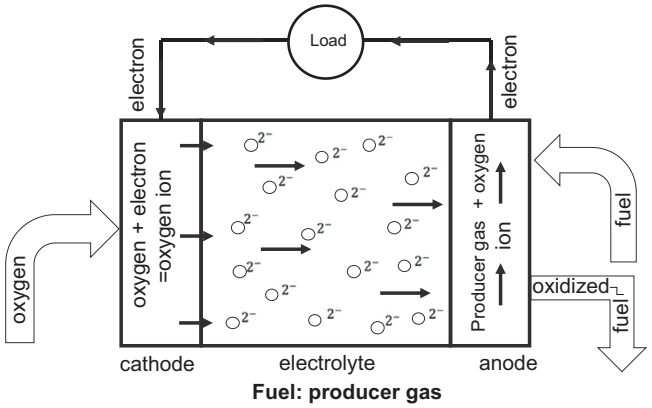

Fig. 3. Schematic of a producer gas fueled SOFC.

Anode side: $CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e^-$ (4)

SOFC operating temperature is usually in the range of 600–1000 °C and the higher temperature of operation improves the cell performance. Further, in the context of power plant, high working temperature is found beneficial as it produces high-grade process heat along with electricity. Simple design with solid electrolyte (porous membrane, unlike liquid in other FCs), and greater fuel flexibility makes SOFC more attractive [16,17]. However, material selection appears to be one of the major issues as high temperature operation needs thermally stable material and that increases the system cost. Further, the anode material for PG fueled SOFC needs special attention for the current material is prone to carbon formation. The following section provides a brief introduction to the materials for different components of FCs, and it may be noted that the issues in using PG is linked mainly to the anode material, while the overall performance of the cell is influenced by others, and hence the materials for all the fuel cell components are briefly described.

3. Material for SOFC components

FC has five major components: anode, cathode, electrolyte, interconnect and sealant, and challenges lie in the material side development for each component has different requirements, while their compatibility is an important issue [21,22]. Any mismatch arising due to thermal expansion coefficient (TEC) among the different components would lead to material degradation [23]. Besides, the need for robust design to have a long-term sustainability at high temperature leading to higher cost is also a major concern. In recent times, efforts have been on to develop materials functioning at intermediate temperatures (600–800 °C) [24–27]. However, complete success has not yet been achieved; low temperature FC has been found to result in significant decline in cell performance mainly due to the increase in internal resistance to the flow of oxygen ions, and also because of a strong cathode polarization [15,23,28]. The following paragraphs provide a brief overview of the most promising materials developed so far for high as well as intermediate temperature (IT) operations. Detailed descriptions on material development can be found in many reports [29–33].

Electrolyte: For high-temperature operation, the electrolyte material that has found wide usage is yttria stabilized zirconia (YSZ): (Yttria replaces Zr^{4+} with Y^{3+} creates oxygen vacancies). While, for IT-SOFC, lanthanum gallate ($LaGaO_3$) doped with strontium on the lanthanum site and magnesium on the gallium site (LSGM), and doped ceria based electrolytes like gadolinium doped ceria (GDC) or cerium gadolinium oxide (CGO) are found attractive. There are a few other materials that also have shown good promises in terms of ionic conductivity and stability, like scandia stabilized zirconia (ScSZ), samarium doped ceria (CSO), nano-composites, etc. [21,34]. However, their applicability is not well established since they are challenged by either of the following factors: (i) high cost, (iii) availability, and (ii) exhibit electronic conduction too [33].

Cathode: As cathode material, strontium doped lanthanum manganate ($La_{1-x}Sr_x$) MnO_3, known as (LSM) and lanthanum strontium cobalt oxide ($La_{1-x}Sr_x$) Co_3 (LSC) are more commonly used. LSM is more preferred due to its better compatibility (TEC matching) with YSZ. [35–37]. However, below 800 °C, LSM exhibits fairly poor catalytic activities for reduction of oxygen, leading to performance degradation of the cell. For low temperature operation, LSC is a good candidate. It exhibits very high electronic and ionic conductivity.

Anode: Ni–YSZ cermet has good chemical stability, and good electronic and ionic conductivity due to Ni and YSZ respectively, and is found to be the most promising material to serve as an anode in SOFC. However, with fuels other than H_2, the problem of carbon deposition is anticipated to occur since Ni catalyzes the C–C bond formation, and it would block the catalytic sites [38,39]. Alternatively, Cu–YSZ or Cu–CeO_2–YSZ can be used as it does not catalyze C–C bonds and shows more tolerance to sulfur contaminants [40,41]. However, it is found that Cu is not as stable as Ni, and because of its low melting temperature and reduced stability at higher temperatures, addition of Cu is applicable only to low temperature SOFCs, at present [29]. Costa-Nunes et al. [42] reported the catalytic activity of Cu could be improved with the addition of Cobalt (Co). Ye et al. [43] reported that a layer of Cu–CeO_2 catalyst on the Ni–YSZ anode surface could suppress the carbon formation to some extent. The role of Ni on carbon deposition is however yet to be clearly understood since carbon formation depends on many other parameters viz., temperature, current density, steam to fuel ratio, etc.

Interconnect: Metals and ceramics are used as interconnect material. Ceramic interconnects are generally used between 800 and 1000 °C, and $LaCrO_3$ doped with strontium or calcium is most commonly used [33]. For low temperature, metallic interconnect, typically chromium (Cr) based alloy and ferritic steels are used. Cr-based alloys are attractive with dispersing of stable oxides but are relatively costly to fabricate.

Sealant: Sealants used are of mainly of two types: compressive and rigid. Generally, for compressive sealant, metal gaskets, i.e. silver, as well as mica-based materials, and for rigid sealant, glasses and glass ceramics are used. Calcium and barium are generally added to glasses so that they exhibit high TEC [44,45]. The advantage of compressive sealant is that they do not require close TEC matching with other SOFC components but during the operation there must be continuous loading. While, rigid sealants, do not require the continuous load, but TEC matching is important.

In summary, exhaustive amount of literature is available on material side for making SOFC working at different temperatures. The use of Ni as the anode material with PG fueled FC is viewed as a major problem for it acts as a catalyst for carbon deposition reactions through CH_4 cracking or CO reduction. Further, the volumetric percentage of carbon compounds in PG varies from 25% to 40%. A detailed study is thus needed to understand the complete chemistry of carbon formation when gases are to be generated from different gasifiers under varying operating conditions. Additionally, further study needs to be directed towards using Cu instead of Ni to establish its benefits especially when operating the cell with PG/syngas generated through gasification.

4. Gasification: technology and issues

4.1. Gasification process

Gasification is a thermo-chemical process wherein biomass/coal with sub-stochiometric combustion in a reactor called gasifier (air/pure oxygen/steam or carbon dioxide as reactant), and the end product is a combustible gaseous mixture of H_2, CO, CO_2 (carbon dioxide) and CH_4. In addition to the gases, gasification results in particulate matter (soot, dust, char and ash), condensable hydrocarbon: tar (a complex mixture of organic compounds formed by aromatics and polycyclic aromatic hydrocarbons (PAH)), alkali metals (primarily potassium and sodium) and some trace gases; hydrogen sulfide (H_2S), hydrochloric acid (HCl), hydrogen cyanide (HCN), ammonia (NH_3), etc. [46].

Box 1 summarizes the major gasification reactions. As evident, H_2, CO, CH_4 are the main products, and the composition of these gases are decided by various factors viz., gasifier types, fuel types, and the operating conditions (e.g. temperature, pressure, gasifying agent etc.) [5]. Table 1 compares the composition and heat value of product gases when air, oxygen and steam as gasifying agent are used.

Among the various gasifying agents, air has been found to have been widely used, with major applications towards power generation using IC engines. While, oxygen and steam gasification result in higher heat value gases and found suitable for advanced applications like turbine, FC, liquid fuels, etc. [50].

4.2. Gasification systems

Gasification system or the reactor configuration can be divided into three main categories (i) fixed bed/moving bed, (ii) fluidized bed and, (iii) entrained flow. Fixed bed can be further classified as updraft, downdraft and cross-draft, depending on the way the gasifying agent is introduced into the reactor. Box 2 summarizes the characteristics of each type.

For biomass gasification, fixed bed configuration is found to have extensive applications, especially in the small scale installations (10–10,000 kW) due to its simple construction [56]. Further, downdraft configuration is found more suitable for power generation due to low tar content [57]. However, for FC application updraft configuration is argued to be useful as the tar laden gas generated from it is expected to contribute to electrochemical reactions through reformation and subsequent oxidization reactions [58–60].

Fluidized bed configuration is appropriate for intermediate units within the range of (5–100 MW) [56]. It has the capacity of handling high throughputs, and it is easy to scale up. However, it has one major disadvantage that it generates the high concentration of tars and particulate matters (10–100 g/N m^3) and also since the gas often carries bed material along with.

Entrained-flow gasifiers are used for large-capacity units, above 50 MW [61]. In coal gasification, this technology largely dominates [57]. While, in the case of biomass gasification, its use is limited, as this type demands a fuel particle size of 100–400 μm which is difficult to achieve [13]. One major characteristic of entrained flow gasifier is that it effectively does not generate any tar. Table 2 presents the tar concentrations in different gasifiers.

Tar, consisting of higher molecular weight compounds, is a major challenge as it has the potential to foul the process equipments or deactivate the catalysts, and as a matter of fact, considerable efforts have been directed to lower its concentration by either scrubbing or by modifying the gasification system and operating conditions [63–66]. Power generators viz., engine, turbine or FC have stringent requirement on gas qualities, and for safe operation, gas cleaning or tar or particulate matter removal is essential [63]. For IC engine, the acceptable limit for tar and particulate matter are specified as < 100 mg/N m^3 and < 50 mg/N m^3 respectively, and for turbine, the particulate matter with size of < 10 μm and level < 30 mg/N m^3 and alkali metal < 0.25 mg/N m^3 are recommended [67]. Molten carbonate fuel cell (MCFC) and Proton exchange membrane fuel cell (PEMFC), the allowable tar concentrations are specified as < 2000 ppmv and < 100 ppmv respectively [66]. For SOFC, however, the limits for various contaminants have not yet been established but would be more stringent. A few researchers have studied the effect of tar on SOFC

Table 1
Composition of producer gas using air, oxygen and steam as oxidizer [47–49].

Oxidizing agent	Gas composition (% vol)					LHV (MJ/N m^3)
	H_2	CO	CH_4	CO_2	N_2	
Air	15	20	2	15	48	5–6
O_2	40	40	0	20	0	10–15
Steam	40	25	8	25	2	13–20
Steam+O_2	32	38	8	20	2	7–8

Box 1–Summary of gasification chemistry.

Zones		Temperature (°C)			
Drying	:	100–200	Moist feedstock + Heat → Dry feedstock + H_2O		
Pyrolysis	:	≥ 250	Dry feedstock + Heat → Char + Volatiles (gases + tar)		
Oxidation	:	1000–1200			***H*** (kJ/mol)
			$CO + ½O_2 \Leftrightarrow CO_2$		−283
			$H_2 + ½O_2 \Leftrightarrow H_2O$		−241.9
			$C + ½O_2 \Leftrightarrow CO$		110.6
			$C + O_2 \Leftrightarrow CO_2$		−393.5
Reduction	:	800–1000	$C + CO_2 \Leftrightarrow 2CO$	(Boudard reaction)	172:5
			$C + H_2O \Leftrightarrow CO + H_2$	(Water gas reaction)	−131.4
			$C + 2H_2 \Leftrightarrow CH_4$	(Methanation)	−74.9
			$CO + H_2O \Leftrightarrow CO_2 + H_2$	(Water gas shift)	−42.3

Box 2–Characteristics of different fixed bed of gasifiers [51–55].

Fixed bed: updraft (countercurrent)	**Advantages**	**Disadvantages**
Biomass and gases move in opposite directions. • Biomass is fed from the top, and oxidizer is supplied from the bottom • Gas is taken out from the top. • Typical exit gas temperature: ~200–400 °C	• Simple design • Fuel flexible • Can take the raw material with high ash content: dry basis < 15% • Can handle fuel with high moisture: wet basis < 50%	• Excessive amount of tar in raw gases • Relatively long start up time
Fixed bed: downdraft (concurrent)		
Biomass and gases move in the same direction. • Biomass is fed from the top and air, and oxygen or steam is supplied either from the top or from the sides. • Gas is taken out from the bottom. • Typical exit gas temperature: ~700 °C	• High quality gas • Suitable for electricity generation	• Moisture sensitive • Not feasible for fuel with low density due to flow problems
Fluidized bed		
• Biomass is brought to an inert bed of granular solids such as sand/dolomite, alumina etc., fluidized by a suitable gasification medium such as air or steam and gasified • Gasification temperature: 750–900 °C	• Uniform temperature distribution across the gasifier owing to high material and energy transfer rate • Suitable for the fuel having high ash content and ash having low melting point	• System is complex • High tar and dust content • Not suitable for fuel having low ash melting temperature
Entrained flow		
• Dry pulverized feed or slurry is fed co-currently with the oxidant, and the flow velocity is high enough to establish a pneumatic transport regime • Unlike fluidized bed, inert solid is not used • Gasification temperature: 1300–1400 °C)	• High temperatures caused by added oxygen nearly destroy oils and tars.	• Cannot handle bigger feedstock, and the process of size reduction is energy intensive • Large amount of molten ash formed during gasification

by considering some model compounds and demonstrated their potential dangers resulting in loss of electrochemical performance [68–70]. The detailed discussion on the effect of contaminants on cell performance is presented in Section 5 of this paper. Hasler and Nussbaumer [63] reported that in mGT, tars are tolerated only in vapor form, and allowable particulate concentration depends on its size, i.e., for the size > 20 μm, the limit is 0.1 ppm, and for 4–10 μm, the same is 10 ppm. Furthermore, mGT requires very low level of HCl (< 0.5 ppm) and H_2S (< 1 ppm) [71]. It is important to mention that there has been considerable progress in the development of cleanup equipment in the last few decades [72–74], and this has widened the applicability of PG to a good extent.

4.3. Some aspects on gas quality for SOFC application

Depending upon the process temperature range, the gas cleanup technologies are classified either hot or cold. Cold gas cleanup generally describes the processes that occur at near ambient conditions, while the hot gas cleanup describes the process between 400 °C and1300 °C or even higher [67]. The equipments for cold gas cleanup are much developed, reliable and less costly, while the hot gas cleanup offers good thermal management [58,75,76]. Many researchers argued that for a system like SOFC where the operating temperature is as high as 800–1000 °C, the cooling of gas for impurity removal, and then subsequent heating for SOFC usage would be a waste of energy [76,77].

While, the argument in support of hot gas cleaning is taking the forefront, herein the authors analyze the scope for cold gas cleaning based on the energy balance and also considering the fouling effect of raw gas. Fig. 4 illustrates the schematic of heat recuperation schemes used in (a) cold gas (b) raw/hot gas to be used in SOFC. The detailed calculations considering two schemes are provided in Box 3.

Table 2
Comparison of tar produced in different gasifier systems [51,62].

Gasifier type	Fixed bed		Fluidised bed	Entrained flow
	Updraft	Downdraft		
Tar range (g/N m^3)	10–150	0.01–0.5	5–40	None

It is evident from Box 3 that in the first case 1 where cold gas cleaning is adopted, the energy that can be recovered from SOFC exhaust is found just sufficient enough to heat up the gases for SOFC usage is up to 800 °C. While, in the second case 2, where raw or hot gases are to be used, the exhaust energy is more than sufficient, and it would be an ideal situation if raw gas could be used directly instead of using cold gas that is to be heated before diverting it into FC. However, the chances of carbon deposition on the anode material increase when impurity laden gases are fed to FC. Cold gas cleaning would be a good alternative to hot gas cleaning provided the energy carried by the exhaust is effectively utilized. Further, the area of the heat exchanger in the case of hot gas cleaning would be much higher and that will add to cost.

4.4. Gasification system with low tar and particulate: experience at the Indian Institute of Science (IISc)

Reduction of tar has always been a challenging issue, and to deal with, many new strategies focusing on primary cleanup: optimization of the operating conditions or designs modification

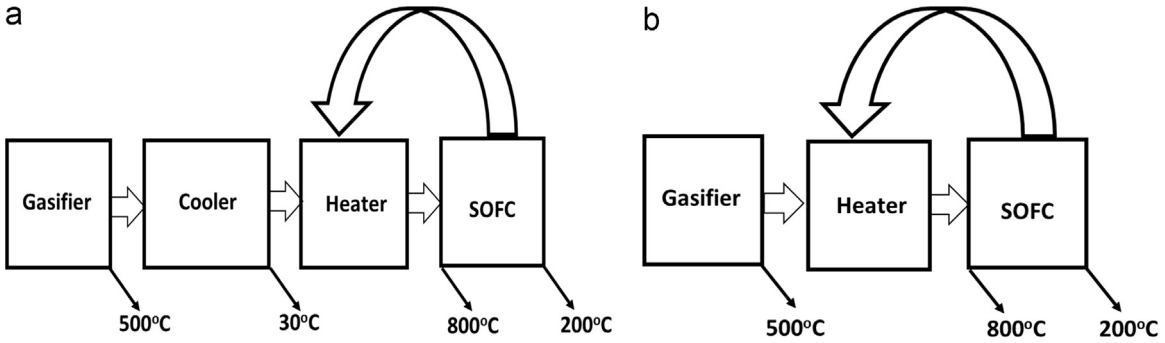

Fig. 4. Schematic showing heat recuperation schemes in SOFC using (a) cold gas and (b) raw/hot gas.

Box 3–Analysis of energy effectiveness of cold and raw/hot gases from gasifier to use in SOFC.

		Case 1	Case 2
		Cold gas cleaning	Hot gas cleaning
Gasifier exit temperature	:	500 °C	500 °C
Temperature after scrubbing and cooling	:	30 °C	–
Heat in the exhaust		2025 kJ	2025 kJ
Heat exchanger effectiveness: (assumed)	:	0.5	0.5
Heat available to preheat the gas for SOFC	:	1012.5 kJ	1012.5 kJ
Energy required for heating gases up to 800 °C	:	1001 kJ	643.5 kJ
Surplus energy	:	11.5 kJ	369 kJ

has come into play [64]. Among the new designs, the two staged gasification system; with separate pyrolysis and reduction zones and the two staged air entry has received broad attention [78–80]. The latter design developed at Indian Institute of Science (IISc) seems more promising from technical as well as economical point of view, and proven effective in fields [81–86]. This system can accommodate both woody and non-woody biomass and gasify them with an efficiency of ~80%. The average gas composition of this system with air as oxidizing agent is found as H_2: 19 ± 1%; CO: 19 ± 1%; CH_4: 1.5%; CO_2: 12 ± 1%; H_2O: 2 ± 0.5%, and the mean calorific value 4.6 ± 0.2 MJ/kg.

The unique feature of the IISc gasification system is that it has dual air entry; one from the nozzle and the other from the top of the reactor. The open top permits the reaction front to move upwards creating a second high temperature zone ensuring high residence time for the gases at elevated temperatures that further facilitates tar cracking due to the simultaneous action of heat and catalytic action of hot char. Detailed measurements have shown that the fraction of higher hydrocarbons in the hot gas in this open top design is lower than that of a classical closed top design. In the raw gas, the respective tar and particulate concentrations are reported to be ~150 mg/m^3, 1000 mg/m^3 respectively, while the same in the cold gas < 2 mg/m^3 and 10 mg/m^3 [48,85]. These low levels of tar and particulates are the main characteristic features that allow the generated gases to use in IC engine, or gas turbine

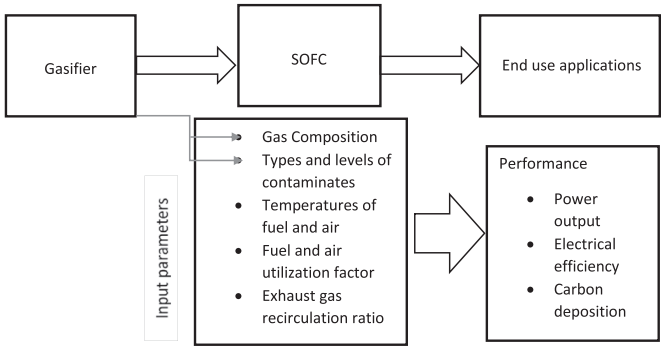

Fig. 5. A schematic representation of various parameters affecting cell performance.

that has stringent norms as stated before. FC has not yet been tested with the gases from this system but can be a good option provided the trace elements remains ineffective to anode materials. The following section consolidates the findings of various researchers who studied the effect of contaminants of PG on performance of SOFC.

5. Progress in PG fueled SOFC technology

Coupling of biomass gasification to SOFC is a relatively new concept and predominantly studied in theory, with a few experimental investigations showing the feasibility of the concept [87–90]. Most theoretical studies aimed at performance evaluation of the system through thermodynamic analysis considering various parameters responsible while experimental investigations focus mainly on the effects of contaminants on the cell performance to establish the minimum allowable limit. Gasification parameters such as steam to carbon ratio, steam to air ratio, temperature, etc. which have influence on gas composition and ultimately the cell performance is also studied by a few researchers [91–93]. The following section includes a review of the work conducted so far, considering different aspects, right from parametric studies to ultimate performance analysis in terms of efficiency.

5.1. *Parametric studies*

Performance of SOFC is dependent on many parameters and some of them are influenced by the gasification process. Types of gasifier, oxidizing agent, operating temperature etc., have a strong influence on the gas composition and it ultimately affects cell output. Fig. 5 illustrates a few input parameters that are found to have a strong effect on the cell performance [94–96]. A few researchers have studied the parameters affecting gasification as

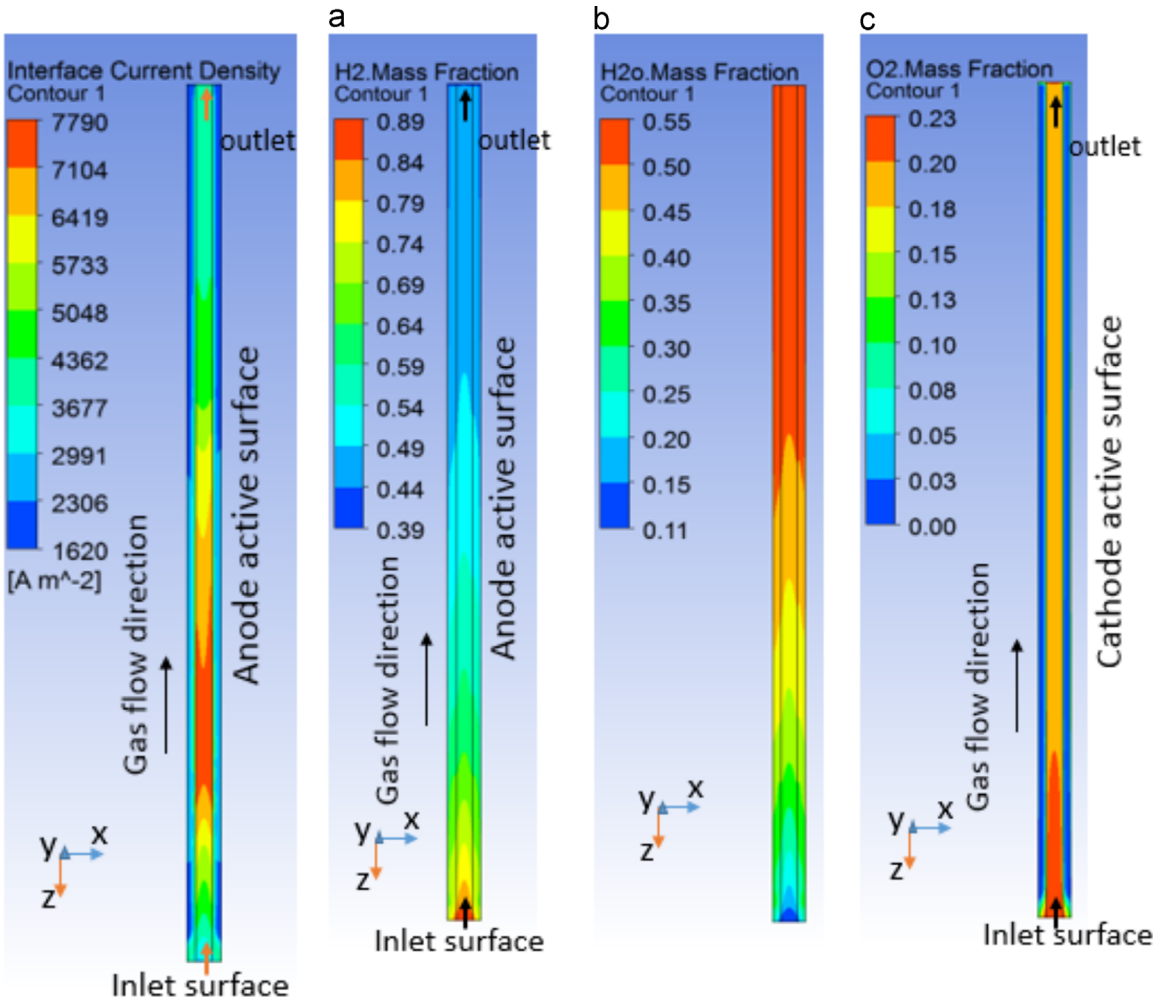

Fig. 6. Distributions of current density and mole fractions of species in a H_2 fueled SOFC.

Table 3
Summary of parametric studies on system performance parameters.

Type of study	Parameters studied	System efficiency (%)	Current density (A/m^2)	Remarks	Ref.
Modeling (0D)	Fuel moisture (%): 40 Fuel utilization (%):70 (allothermal) :95 (autothermal) Fuel moisture (%): 10,30,50 Fuel utilization (%): 65–85	37.7 24.7	3045 2129	(i) Gas composition affects system performance. Higher performance in allothermal system. (ii) With higher fuel utilization, the power output and efficiency increases.	[92]
Modeling (1D)	Fuel moisture (%): 20 Fuel utilization factor: 0.65–0.90 SOFC inlet temperature: 650–850 °C Steam to biomass ratio: 0.5–2 Anode off gas recycle ratio: 0–0.8	~37	4000	(i) Efficiency increases with increase in fuel utilization. Maximum exergy efficiency (67.3%) at the fuel utilization factor of 0.75. (ii) Optimum SOFC inlet stream temperatures: 700 °C (iii) Optimum steam to boiler ratio: 1.5 (iv) Optimum Anode off gas recycle ratio: 0.6.	[94]
Modeling (2D)	Air to steam ratio: 1–6 Preheated air temperature: 50–500 °C Moisture ratio (%): 0–60 Fuel utilization ratio (%): 0.2–0.8	35–52	–	(i) Increase in temperature of air entering the gasification system improves gas composition and thereby average current density (ii) Fuel utilization efficiency and electrical efficiency improve with increase in air to steam mass ratio.	[95]

well as FC processes with an aim to arrive at the optimum values; findings are summarized in Table 3.

Campitelli et al. [92] studied the effect of fuel utilization, and observed that for a fixed moisture content of fuel, increase in fuel

utilization from 65% to 85% resulted in ~25% increase in electric power, ~10% increase in efficiency and ~50% increase in current density. Further, for a fixed percentage of fuel utilization, increase in moisture resulted in higher oxygen requirement and electric power increased by ~35%. However, the reason for increased output is not clear, and a similar study draws opposite conclusion that with increase in moisture content of the wet biomass, the net power output and electrical efficiency decreases [95].

Colpan et al. [95] reported for maximizing power output, the number of SOFC stacks, the mass ratio of air to steam entering the gasifier, and the temperature of the pre-heated air entering the gasifier should be taken as high as possible. They found with increase in air to steam ratio from 1.5 to 6, the useful heat output increased from 40.6 kW to 81.9 kW, and the electrical efficiency by about 5%. Wongchanapai et al. [94] identified four other parameters, steam-to-biomass ratio, SOFC inlet stream temperatures, fuel utilization factor and anode off-gas recycle ratio responsible for cell performance variation, and reported the optimized steam to biomass ratio to be 1.5, anode off gas recirculation of 0.6 and fuel utilization factor to be 0.75.

5.2. Effect of contaminants of syngas on SOFC

The theoretical studies reveal the role of different parameters on cell performance while most of the studies were conducted with only H_2 participating in the electrochemical reactions. However, PG contains carbon compounds as well as several contaminants, and it is important to consider their effects too. Depending on the nature of the contaminants, concentration levels and the mechanism of poisoning, the performance degradation of the cell varies. Certain contaminants cause immediate performance degradation while in most cases, depending on the permissible exposure to the specific harmful species, the deterioration occurs over a long period. So far there is no established limit, and there are discrepancies between the reported values; similar types of FC are found to exhibit different performances due to the differences in microstructure, or diverse operating conditions [68]. The following paragraphs summarize the recent findings.

5.2.1. Studies on tar

The influence of tar – a mixture of higher molecular weight compounds, on SOFC is still being investigated. A few researchers have identified tar to be a potentially dangerous species as it may deactivate the catalyst and lead to carbon deposition on anode, while others have argued that it may contribute to electricity production by reforming and subsequent oxidation, or simply pass through the anode without any substantial effects [58–60]. However, most of the experimental evidences reveal its detrimental effect while performing short/long term tests. Table 4 summarizes the findings.

It is observed from Table 4 that the effect of tar has been studied by considering both real as well as model tar comprising toluene, benzene, and naphthalene, and Ni/YSZ and Ni/GDC as anode materials. Between Ni/YSZ and Ni/GDC as anode materials. Ni/GDC was found to exhibit better performance in terms of carbon formation [97,98]. The extent of carbon deposition is found to vary with the concentration of real tar. Hofmann et al. [99] did not observe any noticeable carbon deposition while studying the effect of real tar with a concentration 1 mg/m^3 on Ni/GDC anode but found a slight deposition when the concentration was 3000 mg/m^3 and the fuel utilization factor was high (~75%). With further higher concentration (10 g/N m^3) however, they did not observe any significant deposition, and this is reported to be due to higher steam content (~75%) and low fuel utilization (20%) [97]. At low steam percentage (2.5% volume), Lorente et al. [97] observed some carbon structures, and they reported it to increase by ~2% when no steam was used compared to when 2.5% steam was used while passing real tar from coal gasification in $H_2/H_2O/N_2$ mixture. Besides, they stated that the reported results were obtained with humidified H_2 gas, in place of syngas for simplicity. The real performance with the combination of higher fuel utilization, low steam flow rate, and real syngas is yet to be uncovered.

With the model tar, however, a number of experimental and a few thermodynamic studies have been conducted, and they reveal the conditions for carbon free operation. However, these studies are not very reliable as carbon deposition was observed above the thermodynamically stable region [93]. Carbon deposition depends on the kinetics of the reaction. Thermodynamic predictions alone cannot be relied upon. Singh et al. [100] reported that carbon deposition decreases with an increase in current density and becomes zero after a critical value. Following this, Mermelstein et al. [98] reported that the critical current density to suppress carbon formation when exposed to 15 g/m^3 benzene would be 365 mA/cm^2. Aravind et al. [101] used naphthalene as a model tar and reported that with 110 ppmv naphthalene, there was no significant impact on the electrochemical performance of Ni/GDC. Mermelstein et al. [98] observed benzene participate through reforming reaction with no performance loss for a period of 30 min. Mermelstein et al. [102] observed negligible impact of benzene (2–15 g/m^3) on the electrochemical performance when the cell operated at a temperature of 765 °C for 3 h at a current density of 300 mA/cm^2. Biollaz et al. [103] observed a minimal performance degradation (1% per thousand hours) when the FC was run for about 1200 h with syngas having tar concentration 5 mg/m^3. Likewise, Martini et al. [104] conducted a test run for about 67 h and found no serious degradation. Dekker et al. [105] evaluated the performance of a syngas fed SOFC with different tar components and concluded that lighter tar compounds, such as toluene, did not affect the cell operation. However, even a lower concentrations of heavier (PAH) compound such as naphthalene, phenanthrene, and pyrene, caused a significant drop in voltage.

In summary, the impact of tars on SOFC anode is still not well understood although the parameters that have a strong influence on carbon deposition are identified. Thermodynamics along with chemical kinetics can provide an estimation of carbon deposition. Experimental evidence is required to establish the effect of real tar when fed at different operating conditions, and for longer duration. Model tar does not reflect the actual condition; besides, thermodynamic analysis gives a wrong picture, with overestimation of carbon deposition.

5.2.2. Studies on particulate matter, H_2S HCl, NH_3

The literature on the influence of contaminants of PG other than tar is scarcely available although they have greater potential to degrade the cell performance by blocking the surface for oxidation. With higher concentration of sulfur, H_2S may be adsorbed at the anode, resulting in inhibiting adsorption of fuel molecules [106–108]. HCl can cause corrosion of the system components. Hoffmann [70] reported a severe deposition of char inside the functional layer of the anode when syngas having char particulates of size smaller than 5–10 μm was fed. Appropriate filtration technologies involving ceramic, or sintered metal filters could however meet the requirement of low particulates.

Matzusaki and Yasuda [109] reported that even 1 ppmv of H_2S can cause a significant performance loss. They also stated that at lower temperature the losses were more severe. Norheim et al. [110] experienced a 2.5% drop in cell voltage with an increase in H_2S concentration from 0 to 100 ppm but no further deterioration with increased concentration (120–240 ppm). However, the

Table 4
Summary of findings of various researchers on impact of tar on SOFC.

Types of study: material	Real tar/Model tar: species	Inlet contaminant conc.	Duration (h)	Operating temperature (°C)	Remarks	Ref.
Thermo-dynamic analysis	Model: 32 species	–	–	600–1200	Increase in current density led to decrease in carbon deposition. The threshold value: 126 mA/cm^2. Minimum carbon deposition at 920 °C.	[100]
Experimental: Ni/GDC	Model: Naphthalene	110 (ppmv)	2	850	Ni/GDC was found to be reasonably tolerant to naphthalene up to a few tens of ppm	[69]
Experimental: Ni/GDC	Real	<1 mg/m^3	150	850	No performance deterioration. Fuel utilization factor: 30%.	[99]
Experimental: Ni–GDC	Real	0–3000 (mg/m^3)	7	850	During testing on high fuel utilization conditions (75%) and high steam content, the SOFC lost performance due to anode nickel oxidation.	[70]
Experimental: Ni–YSZ	Model: Benzene, Toluene, Mixture of naphthalene, pyrene, phenol	15 (g/m^3)	0.5	775	Under similar operating conditions, toluene deposited the least amount of tar followed by tar mix and benzene.	[93]
Experimental: Ni–GDC	Real	0–10 (mg/m^3)	2.5–7	850	Stable performance was achieved for low fuel utilization (20%) and current density 130 mA/cm^2.	[91]
Types of study: SOFC material	Real tar/Model tar: species	Inlet contaminant conc.	Duration (h)	Operating temperature (°C)	Remarks	Ref.
Experimental: Ni/YSZ, Ni/CGO	Model: Benzene	15 (g/m^3)	0.5	765	Ni/CGO anodes were found to be more resilient to carbon formation than Ni/YSZ anodes.	[98]
Experimental: Ni/CGO	Model: Benzene	2–15 (g/m^3)	3	765	Operating the cell at 300 mA/cm^2 over 3 h in a typical biomass gasification syngas with <5 g/m^3 tars did not show the formation of carbon.	[102]
Experimental: Ni/YSZ, NiO/CGO	Real, Model: Tolune	15 (g/m^3)	1	765	Real tar laden gas resulted in lesser carbon deposition than modeled tar, indicating participation of real tar in reforming reaction. NiO/CGO exhibited better performance in terms of degree of carbon deposition.	[97]
Experimental: Ni/GDC	Model: Toluene	15 (g/m^3)	24	700–900	Under the wet conditions Ni/GDC anodes did not suffer from carbon deposition. Use of CO_2 improved cell performance.	[59]
Experimental: Ni/YSZ, Ni/CGO	Real:	13.7–16.7 (g/m^3)	1	765	Ni/CGO presents a better performance (less carbon formation) than Ni/YSZ. Carbon formation was predominantly observed when the anodes were exposed to the lighter fractions as compared to the whole tar sample.	[68]

Table 5
Summary of estimated efficiencies of different gasifier-SOFC configurations.

Concept	Fuel utilization efficiency (%)	Electrical efficiency (%)	Remark	Ref.
SOFC module	50.8	41.8	Highest efficiency was achieved using steam as the gasification agent	[119]
SOFC module	70	36	Integration of a SOFC with a allothermal biomass steam gasification process into a CHP system is established	[122]
SOFC module			Better heat management in the hot gas cleaning process results in higher system efficiency.	[76]
(i) Hot gas cleaning	50	23		
(ii) Cold gas cleaning		21		
SOFC module	85		Electrical efficiencies of the gasifier-SOFC-CHP systems with different gas cleaning systems are almost the same.	[59]
(i) Combined high and low temperature gas cleaning system		25		
(ii) High temperature gas cleaning system		23		
Gasifier-micro-gas turbine (mGT)	85	28.1	Highest efficiency in the hybrid system	[117]
Gasifier-SOFC		36.4		
Gasifier-SOFC-micro-gas turbine (mGT)		50.3		
(i) Decentralized biomass-SOFC CHP plant	85	44.9	Efficiency is higher in decentralized biomass-SOFC CHP plant	[121]
(ii) Decentralized biomass CHP plants		30–34		
SOFC module	85	38.0	Higher efficiency in the hybrid system	[118]
SOFC– mGT		50.8		
SOFC–GT	80	Exergy efficiency (%)	High temperature gas cleaning results in a slightly higher performance (0.5%) compared to low temperature gas cleaning.	[77]
(i) large scale steam gasification coupled with low temperature gas cleaning		49.3		
(ii) large scale air gasification coupled with low temperature gas cleaning		49.4	Large scale systems have a higher efficiency than small scale systems, due to larger exergy losses	
(iii) air gasification coupled with high temperature gas cleaning		49.9		
(iv) a small scale system based on air gasification and high temperature gas cleaning		46.0		

duration of exposure was only 1 h, and the effect might be different for long term operations. Aravind and Jong [75] demonstrated that for short term operation, the performance of the SOFCs with Ni/GDC anodes is not affected by a few ppmv of H_2S. The effect of other contaminants like alkali, HCl, NH_3, HCN, etc., of syngas is not yet studied much, although they may have serious consequence on cell performance in long term operation. For short-term operation, NH_3 is reported to be harmless, while a few hundred ppmv of HCl was found to result in larger performance loss [69,111,112]. The rest of the contaminants especially, the alkali vapor like sodium or potassium are scarcely documented but may have a severe impact on the cell performance when operated for long.

5.3. Theoretical studies involving performance evaluation of PG/syngas fed SOFC

Researchers have investigated the possible aspects of combining FC with other energy conversion technologies such as gas turbine or steam turbine (ST/GT) so that its performance be improved. Hybrid systems like mGT, or combined/hybrid mGT/FC, etc., are already conceptualized, and they are expected to show much higher efficiencies than a FC alone [113–115]. A system with gasifier-SOFC-GT components is expected to have an electrical efficiency of about 50–60%, even at low power levels [75]. Further, FC module generates higher efficiency than IC engine that at present is most widely used for small-scale power generation due its simpler construction and lower capital cost [9,13]. Table 5 summarizes the estimated efficiencies of a few different modules designed for electrical power generation.

Athanasiou et al. [116] analyzed the integrated SOFC-ST system, and they found the electrical efficiency of the system to be 43.3%. Bang-Moller and Rokni [117] carried out a modeling study of three combined heat and power systems based on biomass gasification. In the first system, product gas is converted in mGT, the second system involves a SOFC, and the third system involves an integration of SOFC with mGT. It was reported that the third system resulted in the highest electrical efficiency: 50.3% against 36.4% and 28.1% for the second and the first system. Sucipta et al. [118] investigated performance analysis of a tubular SOFC-mGT system fueled with syngas coming from air gasification, oxygen gasification, and steam gasification, and the highest efficiency was recorded in the case of steam gasification, both for the SOFC module (38%) and the hybrid system (50.8%). Similar result was reported by Colpan et al. [119] who studied a 10 kW SOFC with different gasification agents: air, enriched oxygen and steam, and the resulting electrical efficiency in case of steam as oxidizer was 41.8%.

Liu et al. [120] studied a 5 kW SOFC CHP (combined heat and power) system with various gas cleaning solutions: a combined low and high temperature gas cleaning system and a high temperature gas cleaning system, and reported that irrespective of the techniques, the electrical efficiency of the CHP system was approximately the same. However, the high temperature solution showed higher thermal efficiency both in the energy and exergy balance. Bang-Moller et al. [121] developed a mathematical model to predict the performance of a decentralized CHP plant, combining a two-stage biomass gasification and a SOFC and predicted the electrical efficiency to be 44.9%, against 30–34%, in the case of traditional decentralized biomass CHP plants.

In a simulation work carried at the Indian Institute of Science (IISc) as a part of Master's thesis [122] a fluid dynamic SOFC model was developed using CATIA-V5 as a modeling tool and ANSYS ICEM CFD as a meshing tool. An in-house developed SOFC module to handle the electrochemistry was integrated with the standard ANSYS FLUENT solver for the simulation of a single cell of a fuel cell stack. The developed model and the simulation strategy has been validated with literature reported data for H_2 as a fuel [123]. Various factors like the average current density, fuel utilization factor, etc. compare well between the simulation and reported data. As a typical example, (Fig. 6) presents the current density distribution along the electrode surface. The simulation indicates a peak current density of 7790 A/m^2 with 95% volume fraction of H_2 and 5% H_2O. This is consistent with an area average current density as cited by Qu et al. [123]. Further, the H_2 validated model is extended for PG fueled operation. Fig. 7 presents the current density distribution and mole fraction variations at the electrode

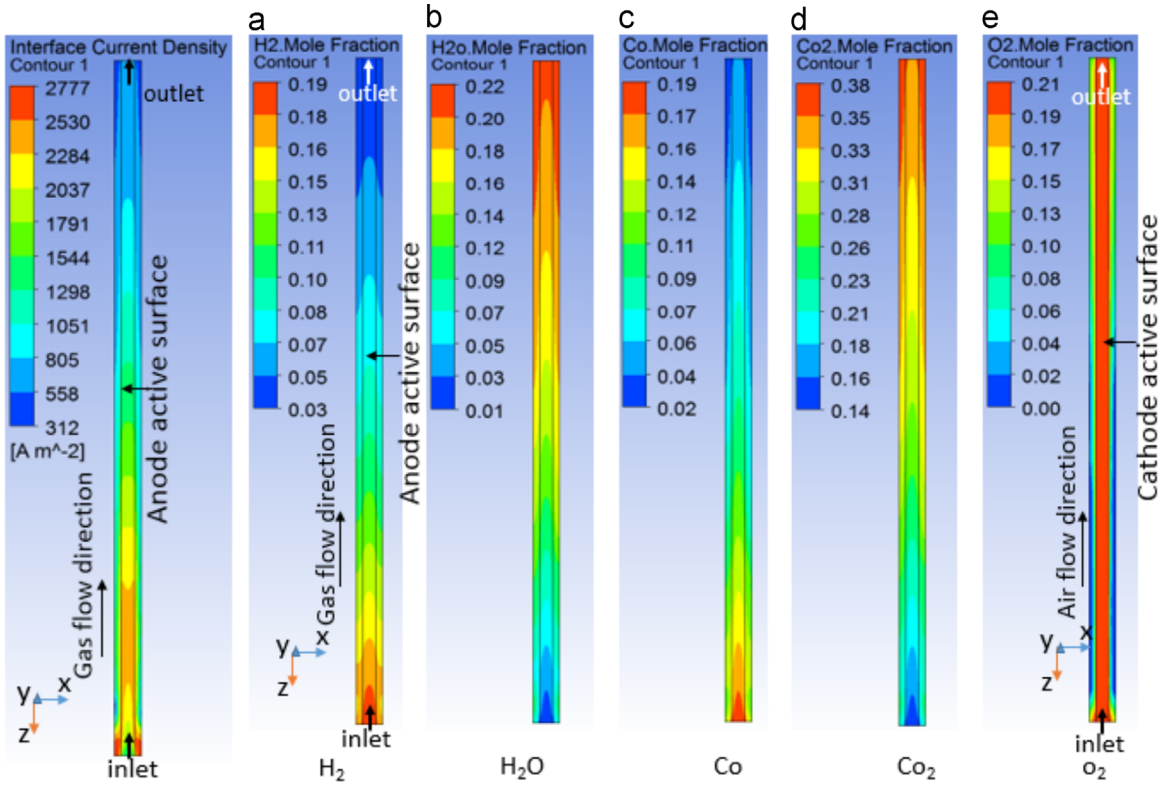

Fig. 7. Distributions of current density and mole fractions of species in a producer gas fueled SOFC.

Table 6
Performance of gasifier-IC based power plants.

Gasifier type	Biomass type	Oxidant	Cleanup system (hot/cold)	Power output (kW)	Electrical efficiency	Ref.
Down draft	Wood chips	air	cold	30	20.0	[128]
Down draft	Rice hull	air	cold	200	12.5	[129]
Circulating fluidized bed	Rice hull			1000	17.0	
Downdraft	Wood	air	cold	100	18.0	[9]
Down draft	Agro for-estry residues	air	cold	50	15.0	[130]
Circulating fluidized bed				67–75	16.0	
Down draft	Pine	air	cold	11.7	23.0	[131]

Table 7
SOFC performance comparison with pure hydrogen and hydrocarbons [132].

Fuel	Open circuit voltage (mV)	Power density (mW/cm^2) (max)	Current density (mA/cm^2) (max)
H_2	785	114	508
CH_4	770	107	490
C_2H_6	763	105	488
C_3H_8	801	128	430
C_4H_{10}	812	085	338

surface for PG with composition: H_2: 20%, CO: 20% CH_4: 2%, CO_2 :10% and rest N_2 for a single cell. The simulation indicates a peak current density of 2777 A/m^2 with a utilization factor (estimated based on the mole fraction of CO and H_2) of 82%. With the current density being proportional to the number of active moles supplied, the reduction in peak current density for PG as compared to H_2 is along the expected lines.

Panopoulos et al. [124,125] studied the feasibility of high efficiency SOFC-CHP systems of sizes up to 1 MWe with a novel allothermal biomass gasifier using steam as the gasification agent, and reported the electrical and exergetic efficiencies to be 36% and 32% respectively. Cordiner et al. [126] simulated a 14 kW SOFC coupled with a downdraft gasifier by means of a zero-dimensional equilibrium model for gasifier and a 3D CFD model for the SOFC and computed the electrical efficiency of the system to be 45.8%. Table 6 enlists the efficiencies of a few gasifier-IC engine systems reported by Bocci et al. [127].

Summarizing, it can be stated that FC when combined with another energy generator like turbine results in higher electrical efficiency. However, to confirm the fact, it has to be established experimentally. Theoretical studies involve many assumptions viz., FC is insulated and operates at steady state, only H_2 is electrochemically reacted, etc., and these parameters may have significant influence in real sense.

5.4. Performance comparison of SOFC with different fuels

SOFC is fuel flexible, and hence it has been tested with various kinds of fuels by different researchers. A few have compared its performance with the base fuel H_2 and reported that change of fuel does not have a significant influence on the performance of the cell while the use of carbon based fuel is of a concern. Table 7 presents the results of Madsen and Barnett [132] where they report the open circuit voltages (OCV), power densities and the current densities of different hydrocarbons viz., H_2, CH_4, C_2H_6, C_3H_8, and C_4H_{10}, as well as pure H_2.

It is observed that the OCV for pure H_2 as well as for hydrocarbons is nearly same ~800 mV, and the maximum power density ~100 mW/cm^2. The maximum current and power densities are appeared to vary slightly with the fuels molecular weights. However, it is reported to be due to the experimental artifact; no significant differences are observed when hydrocarbons are used

Table 8
SOFC performance comparison with pure and diluted hydrogen [133].

Fuel	OCV (v)	Power density (W/cm^2) (max)	Limiting current density (A/cm^2)
H_2	1.05	1.7	4.2
H_2–He (He concentration: 15–78%)	0.9–1.0	0.75–1.5	1.5–4.0
H_2–N_2 (N_2 concentration: 15–80%)	0.9–1.0	0.5–1.5	0.9–3.7
H_2–CO_2 (CO_2 concentration: 15–81%)	0.85–0.95	0.4–1.3	0.6–3.5
H_2–H_2O (H_2O concentration: 15–80%)	0.85–.0.95	0.6–1.4	0.9–3.6
H_2–CO (CO concentration: 14–80%)	1.0	1.0–1.6	2.0–3.5

in place of H_2. However, considerable differences are observed when CO is used in place of H_2. Jiang and Virkar [133] observed the maximum power density for CO as fuel: 0.7 w/m^2 against 1.7 w/m^2 for pure H_2 in Ni–YSZ anode. Costa-Nunes et al. [42] observed similar performance with H_2 and CO fuels in a cell with Cu–CeO_2–YSZ anodes. Slow diffusion and electrochemical reaction rates of CO than H_2 are the cause behind the lower maximum power and current densities. Jiang and Virkar [133] however observed a comparable performance with pure H_2 when CO was used in combination with H_2, even when CO concentration was as high as 55% due to additional H_2 produced through water gas shift reaction Further, they reported about variation of electrochemical parameters when pure H_2 was replaced with diluted H_2 (diluents: He, N_2, CO_2, H_2O in varying concentrations ~15–80%) due to higher concentration polarization at higher concentration of the diluents (Table 8). Norheim [134] compared the performance of SOFC with PG and natural gas and reported similar behavior (OCV: 900 mv) for all the conditions tested.

In summary, the use of PG in place of H_2 in FC shows a promising approach as the electrochemical behavior of this fuel is found similar. However, contamination of anode material is still a major issue and needs a critical evaluation. There are arguments related to the use of raw gas, but the degree of degradation of the electrode is of serious concern compared to the trade of on efficiency improvement by a few percentage points. As indicated earlier, the authors believe that it would be the desirable condition to eliminate any contaminant before ingression of gas in the SOFC as there it would help to maintain the anode side clean without any fouling.

6. Conclusions

In summary, the coupling of biomass derived PG with high-temperature SOFC is an active area of research with clear efforts on the development of newer material to support impurity laden fuel without noticeable cell degradation, and behavior of the contaminants with the current existing materials. The progress made in the last few decades is noteworthy, however, the scope for commercialization is still unclear, for durability of the technology is challenged by few technical issues focusing on the appropriate material, gasification technology, cleaning of contaminants, etc. exists and need serious attention.

From the material perspective, challenges lie in developing chemically and thermally stable anode materials without being indulged into carbon deposition and facilitating long term operation. There is a need to carry out detailed investigations on the reaction mechanism and kinetics at each electrode, electrolyte, electrode/electrolyte interface and determine the degradation mechanism. Impacts of various contaminants on the existing Ni–YSZ or Ni–GDC anode are to be largely explored while the chemistry with newer probable material like Cu is to be well understood. The short term and long term effects of the trace contaminants to be uncovered, and the tolerance limits of various contaminants are to be identified for fixing the requirement on the fuel side. It is observed that the current literature does not provide a clear picture on the set limit for different contaminants, and discrepancies are believed to due to the differences in electrode material, microstructure differences and diverse operating conditions.

In the modeling context, fluid and electrochemistry coupling is established and typical power density, overall efficiencies, etc. are predicted with good accuracy. Thermodynamic studies are found to provide some insights into carbon free operating conditions while experimental study rules out its reliability for carbon deposition as it was seen to occur above the thermodynamically stable region, and this establishes the need for comprehensive experiments uncovering the chemistry. Correct of knowledge on the behavior of the contaminants with SOFC components would help to specify the requirement of gas cleaning systems and designing the system with an economic viability, unlike the current hot gas cleanup technology. Utilizing the process heat, and acquiring better understanding on the interactions between the various species in PG and SOFC anodes would be the main criteria in lowering the cost and establish the durability of the technology.

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