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SOFC power generation system by bio-gasification

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Abstract

Power generation using SOFCs, is one of the technologies that can reduce emissions, allow fuel flexibility and achieve high efficiencies. Combining gasifiers with SOFCs would make it possible to extract energy from biomass with lower environmental impact compared to conventional fuel based systems. The hybrid SOFC-gasifier system is best suited for application in standalone systems. The present study shows the performance of a hybrid SOFC for different types of biomass feed. The gasifier reactions are simulated using AspenPlus and a 1D mathematical fuel cell model is used for calculating the SOFC performance. Amongst different biomass fuels chosen in our study, sugarcane bagasse shows best performance in hybrid SOFC. The electrochemical performance of the biomass feed hybrid SOFC is found to be less compared to a hydrogen fuelled system. The advantage of the hybrid system is that since energy generation is dependent on biomass feed, energy sustainability can be attained with proper policy and management.

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1. Introduction

Usage of hydrogen and carbon monoxide rich syngas from biomass gasifier for power generation through solid oxide fuel cell (SOFC) is a promising 'clean energy' technology which has environmental and economic benefits. [1]. Kivisaari et al. discussed the feasibility of integrating a 50 MW fuel cell system with an entrained flow coal

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gasifier which resulted in an overall electrical efficiency of about 47% and an overall efficiency close to 85%. [2] Doherty et al. modeled a 100 kW tubular SOFC and biomass gasifier integrated system in AspenPlus and investigated the effects of varying the fuel utilization factor, current density and steam to carbon ratio on SOFC stack performance [3]. Carlo et al. simulated a cogeneration system with a fluidized bed gasifier coupled with SOFC and micro gas turbine [4]. The results were validated against experimental data available from literature. Athanasiou et al. examined the efficiency of incorporating an SOFC in the conventional biomass gasification turbine process. It has been concluded that the integration increased the overall efficiency of the gasifier-SOFC-turbine system up to 62% of the heating value of the biomass feed; while gasification-turbine systems can reach only 40 % [5]. Toonssen et al. reported that air gasification system integrated with an SOFC gives overall electrical exergy efficiency of 49.9% [6]. An interesting thing to be noted in their study is gasification medium did not influence the overall efficiency of the process. Instead, the temperature of the gas cleaning has been found to affect the efficiency. It is found that in the reported works; the emphasis is mostly on developing an approach which concerns either the gasifier or fuel cell in detail. Efforts to combine both the models and using different biomass feeds as input has been lacking in most studies.

This work concerns with analyzing the performance of the SOFC when different biomass feeds are introduced in the SOFC gasifier hybrid system. The gasification reactions are simulated in AspenPlus and the process conditions are optimized for maximum hydrogen and carbon monoxide output. The output conditions, such as gas composition and temperature of the syngas are used as input for mathematical model of SOFC. The mathematical model is used to predict the current density and power density characteristics of the SOFC.

2. Methodology

2.1. AspenPlus modeling approach

Gasification of the biomass is carried out using an air gasifier. The reactions involve volatile combustion as well as gas-solid reaction regimes. The heterogeneous and homogeneous reactions follow complex kinetics and they are often dependent on hydrodynamics of the reactor configuration used. Many researchers have attempted to develop kinetic model for these reactions [7-9]. Hence, for the sake of simplicity, a kinetic free equilibrium model has been developed.

2.2. Assumptions

The gasification process is assumed to be isothermal and steady state. Volatile combustion reactions and gasification reactions could be achieved by kinetic free equilibrium model. Devolatilization of biomass takes place instantaneously and the volatile components are predicated by proximate analysis of the biomass. The carbon in vapor phase is treated as pure carbon and the residual char mainly consists of pure solid carbon and ash. Gasification operation is modelled in three stages: decomposition of biomass, volatile combustion and gasification as shown in Fig. 1.

- I. Biomass Decomposition: *RYield Block* Biomass is treated as a non-conventional feed in AspenPlus. RYield block in AspenPlus is used for converting nonconventional feed to conventional components (C, H,O,N,S,Cl,Ash) which can be processed by AspenPlus with the help of user subroutine. The decomposition heat is integrated forward using heat stream Q1.
- II. Volatile reactions:
 - Sep block With the help of proximate and ultimate analysis Sep block splits the components into volatile and solids with the help of user subroutine.
 - RGIBBS block RGibbs model assumes Gibbs free energy minimization to determine the composition of each phase. This model is used when reaction stoichiometry is not known but reactors temperature and pressure are known. The products of volatile homogeneous combustion reactions are defined by Gibbs equilibrium using this block in AspenPlus.
- III. Gasification reactions: Considering a kinetic free model RGibbs reactor block is used to simulate gasification reactions. RGibbs simulates these reactions by simultaneous phase equilibrium and chemical equilibrium.

Volatile combustion reactions are highly exothermic and this heat is utilized for endothermic gasification reaction using forward integration of heat stream Q2.



Fig. 1.: AspenPlus flowsheet of biomass gasifier (a) Simulation model and (b) Simulation calculation procedure

2.3. SOFC model

The hybrid SOFC performance depends on the electrochemical reactions occurring inside the SOFC. The polarization curve of such a fuel cell can be chosen as performance indicator. While the losses are typically same in nature as traditional SOFCs, the magnitude of activation and mass transport losses varies depending on the fuel choice. The SOFC anode is directly coupled to the exhaust from the gasifier. The typical constituents of the gas fed to the SOFC contain H_2 , CO, CO₂, N₂, H₂O and CH₄. Among these, hydrogen and carbon monoxide can be electrochemically oxidized within the fuel cell. For the two component fuel mixture, the reactions are assumed to occur in parallel with each other. The oxygen reduction reaction occurs in series with the reaction at anode in such a manner that the anodic and cathodic charge generations are same. The SOFC hydrogen and CO electrochemical reactions can be summarized respectively as:

Anode:
$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$
 (1)

$$\mathcal{C}\mathcal{O} + \mathcal{O}^{2-} \to \mathcal{C}\mathcal{O}_2 + 2e^- \tag{2}$$

$$Cathode: O_2 + 2e^- \to O^{2-} \tag{3}$$

Net Reaction:
$$2H_2 + O_2 \leftrightarrow 2H_2O$$
 (4)

$$2CO + O_2 \leftrightarrow 2CO_2 \tag{5}$$

2.3.1. Assumptions

The individual cells in the SOFC system perform similarly and the cell voltage in each cell is nearly the same. The current generation is constant over the entire electrode. For an SOFC operating with fuel mixture, the total current generation is determined as a summation of the individual currents resulting from the reaction of each species in the fuel mixture. For the hybrid SOFC, each mole of reacting hydrogen and carbon monoxide produces two moles of electrons. Thus, the theoretical maximum voltage that can be achieved by this kind of cell operating on either specie is:

$$\mathbf{E}_{g}^{i} = -\frac{\Delta g_{f}^{i}}{2\mathbf{F}} \tag{6}$$

Here, Δg_f^i is the maximum electrical work that can be produced per mole of reactant and F is the Faraday's constant. However, the reversible cell voltage that is observed has a lower value. The loss is due concentration polarization and is dependent upon partial pressures of the reactants, temperature and operating pressure of the fuel. It is described using the Nernst equation and can be separately obtained for the two oxidation (H₂ and CO) reactions. This approach is suitable because the reactions are independent of each other. Fig. 2. is a representation of the current generation (i_{H2} and i_{CO}) and their corresponding losses for the fuel cell. The two oxidation reactions occur in parallel with each other and in series with O₂ reduction. It is to be noted that the overpotential of CO oxidation is 2-3 times greater than H₂at the same current density [10]. It was found that this aspect could not be explained solely on the basis of mass transport losses of the species [11].Hence, in this work the exchange current density of CO oxidation is modified instead. The total current i_{Total} generated from the anode and cathode of the cell is used for calculation of the ohmic overpotential. The losses are explained in detail in the following section.



Fig. 2.: Circuit diagram for the different losses.

2.3.2. Activation loss

The activation loss is caused by activation polarization and is a major contributor to total voltage loss at low current densities. The loss can be expressed by the Butler-Volmer equation:

$$J = J_0 \left[\exp\left(\alpha \frac{n_e F}{RT_s} V_{act,i}\right) - \exp\left(-(1-\alpha) \frac{n_e F}{RT_s} V_{act,i}\right) \right]$$
(7)

The activation energy at a particular current density is $V_{act,i}$. The exchange current density (J₀) depends on the mole fraction of the ith species and the reaction order as per the relation proposed by Zhu et al. [12]:

$$J_{0} = J_{0}^{0} \prod_{i=1}^{n} X_{i}^{\gamma_{i}}$$
(8)

Here, J_0^0 is a constant and γ_i is the exponential factor. The exchange current density is determined separately for the anode and cathode sides depending upon the local gas composition in the TPBs.

$$V_{act} = \frac{2 RT}{nF} \left(\sinh^{-1} \left(\frac{i}{2i_0^a} \right) + \sinh^{-1} \left(\frac{i}{2i_0^c} \right) \right)$$
(9)

2.3.3. Ohmic loss

The conductivity of materials used as cell components, thickness of the different layers, contact resistance between components, operating temperature and the current drawn from the cell are the factors that govern the ohmic loss of an SOFC. On assuming ideal contact between all cell components, the contribution of contact resistance can be neglected and the expression for the loss becomes.

$$V_{\rm ohm} = \left(\frac{\delta_{\rm a}}{\sigma_{\rm a}} + \frac{\delta_{\rm c}}{\sigma_{\rm c}} + \frac{\delta_{\rm el}}{\sigma_{\rm el}}\right)i\tag{10}$$

Here, δ_j is the thickness of each corresponding layer and σ_j is the respective conductivity. The conductivity correlations are used from reference [13].

2.3.4. Mass transport loss

The reactants travel from the flow channels, across the porous electrodes and reach the site of the reaction in the TPB. The mode of transport for species is primarily diffusion and in SOFCs, the process is aptly described by an effective diffusivity co-efficient. This co-efficient is obtained by taking into consideration both molecule-molecule (Stefan Maxwell equation) and molecule-wall collision (Knudsen diffusion). It has been widely adopted in many studies and found to have a good agreement with experimentally determined values. The binary diffusivity values and the Knudsen diffusion co-efficient are obtained from reference [14].

$$\nabla C_{i} = \frac{J_{i}}{D_{iKn}^{eff}} + \sum_{j=1, j \neq i}^{n} \frac{C_{j}J_{i} - C_{i}J_{j}}{C_{T}D_{ij}^{eff}} + \frac{C_{i}}{D_{iKn}^{eff}} \frac{B_{g}}{\mu} \nabla P$$
(11)

The third tern in Eq. (11) can be neglected as the pressure drop in the pore is negligible. With this simplification, Eq. (11) can be solved using numerical method and the concentration of species can be obtained at the TPBs. The concentration of each species being known in both the bulk and the TPB, Eq. (12) is employed to determine the concentration loss.

$$V_{\rm con} = \frac{{}_{\rm RT}}{{}_{\rm F}} \ln \frac{{}_{\rm C_i}}{{}_{\rm C_0}} \tag{12}$$

The concentration gradient of the species across the porous region is proportional to the species consumption/generation rate n_i at the TPB, which can be co-related with the local current generation J_i .

$$n_i = \pm \frac{J_i}{nF}$$
(13)

In the current work, the diffusion is modelled as a one dimensional process and the gas concentration is assumed to be uniform in the direction of reactant flow in the gas channels. The boundary condition used while solving the diffusion equation is based on specification of bulk concentration of reactant and its corresponding concentration at the TPB. The other relevant parameters for the fuel cell model are mentioned in Table 1.

Fabl	e 1:	SOF	C	model	parameters
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Setting Parameters	Values
Operating temperature	800 C
Anode thickness	1.5 mm
Cathode thickness	100 µm
Electrode thickness	50 µm
Pore diameter	1 µm
Porosity/Tortuosity ratio	0.1
Exchange current density at anode	55 A m ⁻²
Exchange current density at cathode	7500 A m ⁻²
Faraday constant	96485C/mol
Reference pressure	1 atm

3. Results and discussion

The performance of the hybrid fuel cell system can be assessed from two different perspectives; capacity and performance. Capacity indicates at the flow rate of gases that is produced as output from the gasifier. It is calculated by taking a feed rate of 100 kg hr⁻¹as gasifier input for each biomass type and simulating the gasification reaction using AspenPlus. The biomass feed material chosen in our study holds importance from an Indian context and the

		Cattle	Sugarcane	Coconut	Rice		Sewage
		feed	bagasse	shells	husk	Starch	sludge (dried)
Proximate analysis	MC^*	13.88	50	5.6	11.2	16.76	3
	Ash	13.67	2.1	0.47	18.29	0	44.2
	VM**	60.52	37.9	71.84	48.31	75.26	46.56
	FC***	11.94	10	22.09	22.2	7.98	6.24
Ultimate Analysis	С	39.09	22.05	49.41	27.92	36.84	28.13
	Н	4.61	2.63	6.2	4.23	5.68	3.69
	Ν	0.83	1	0.28	0.49	0	3.01
	S	0.25	0.02	0.75	0	0	0.78
	0	26.68	22.2	37.29	37.86	40.73	17.03
	Cl	0.99	0	0	0	0	0
	Ash	13.67	2.1	0.47	18.29	0	44.2

proximate ar	nd ultimate	analysis o	of the	data is	shown	in Table 2.
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MC^{*}- *Moisture Content; VM*^{**}-*Volatile Matter; FC*^{***}- *Fixed Carbon*

Owing to their varying carbon and moisture content, the hydrogen and carbon monoxide flow rates vary with change in biomass feed. As shown in Fig. 3, coconut shell gives the maximum amount of carbon monoxide flow rate and hence the syngas procured from its gasification has maximum calorific value. It is also clear from the ultimate analysis data in Table 2 that coconut shell has maximum amount of carbon and hydrogen associated with it.



Fig. 3.: Hydrogen and carbon monoxide flow rate for different biomass feed masterial

The effect of reactor temperature on hydrogen and methane flow rate has been calculated using sensitivity analysis tool in AspenPlus. The plot of gas flow rates against reactor temperature is shown in Fig. 4. It is clear that the flow rate of methane i.e. the fraction of methane in the syngas wanes as the reactor temperature increases while hydrogen flow rate increases up to a certain temperature and stays constant thereafter. The optimum temperature for maximum hydrogen fraction has been found out to be ~1100 K. It is typically the temperature at which SOFCs are operated.



Fig. 4.: Effect of reactor temperature on Methane and hydrogen flow rate

The fuel derived from the different biomass sources are used as input in a hybrid SOFC and the mathematical model is used to calculate its performance characteristics. It is found that the amongst the different biomass resources, sugarcane bagasse (H₂:CO mole fraction of ~ 9:1)gives the best performance (0.58 W cm⁻²at 0.42 V). Under similar operating conditions, an SOFC running with pure (99%) H₂ is found to produce a power output of 0.6 Wcm⁻². A higher percentage of CO in the fuel mixture generally causes substantial decrease in performance decrease of SOFC has been observed forthe biomass feeds used in our study. This can be attributed to the high H₂:CO mole fraction amongst all biomass inputs. In this case, a power output of 0.56 W cm⁻² has been obtained which is ~ 6.67% less than the power density obtained by using pure hydrogen. Other biomass feeds have H₂:CO ratios intermediate to that of sugarcane bagasse and coconut shells and consequently, the power density obtained using these feeds will have intermediate values. It can be concluded that the output of gasifier using any of the possible biomass feeds mentioned in Table 2 can be coupled with SOFCs for power generation.



Fig. 5.: Comparision of performance of hybrid SOFC using two different biomass derived fuel with a fuel celloperating with pure H₂.

4. Conclusions

Hybrid SOFC is a promising technology for harnessing energy from biomass due to its immunity to fuel purity. A wide range of biomass is explored in this work as gasifier feedstock. The gas flow rate and composition from gasifier has been determined using AspenPlus toolbox. It is found that coconut shells produce highest output of hydrogen and carbon monoxide amongst all the biomass resources when the gasifier input flow rate is kept constant.

A mathematical model is used to predict the performance of the fuel cell when fed with H_2 -CO mixture. From the point of view of performance, when gasifier output is combined with SOFC, sugarcane bagasse is found to give good performance and coconut shell shows least power density. The power density values obtained are 0.58 W cm⁻² and 0.56 W cm⁻² for sugarcane bagasse and coconut shell respectively. As the other biomass options have H_2 -CO composition intermediate to that of sugarcane bagasse and coconut shell, their performance lies within their power density range. The study demonstrates that it is possible to achieve reasonably good performance with a hybrid SOFC system for different types of biomass as input.

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