

Bioethanol-Fuelled Solid Oxide Fuel Cell System for Electrical Power Generation

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1. Introduction

Tremendous consumption of energy to serve daily lives and economic activities has led to the critical problem of energy shortage since the current main energy sources rely on fossil fuels which are non-renewable. Therefore, efficient renewable energy sources need to be investigated and improved to replace or substitute the use of fossil fuels to alleviate environmental impacts while being sustainable. Biomass-derived fuels are recognized as promising alternatives among other renewable sources e.g. wind, solar, geothermal, hydropower, etc. This fuel can be produced from various available agricultural materials, hence there is no problem of feedstock supply. Instead, its use is beneficial for those countries having strong background in agriculture. In addition, this agro-based fuel can provide a CO₂-closed cycle as the CO₂ released from the fuel combustion can be redeemed with the CO₂ required for biomass growth. Bioethanol plays an important role as a promising renewable energy among other biofuels due to its useful properties such as high hydrogen content, non-toxicity, safety, ease of storage and handling (Ni et al., 2007). An efficient energy conversion system is required to maximize bioethanol fuel utilization to obtain a full performance. Combustion heat engines which are widely used nowadays have a low conversion efficiency of power production due to losses during multiple energy conversion stages as well as a low value of chemical energy of bioethanol represented by LHV or HHV compared to those of fossil fuels (C₆ hydrocarbons or above). Moreover, electrical energy efficiency produced from a combustion heat engine becomes even lower because of further losses from more energy conversion stages. Fuel cell technology is considered to be an interesting alternative for efficient energy conversion since it can directly convert chemical energy stored in the fuel into electrical energy via electrochemical reaction. Less energy is lost in the fuel cell operation and higher electrical efficiency can be obtained. However, the problems in using fuel cell technology such as short-life operating time, high manufacturing cost and impromptu infrastructure support are still issues to be tackled. The Solid Oxide Fuel Cell (SOFC), a type of fuel cells, is selected to be an electrical

power generation unit fuelled by bioethanol because of its outstanding characteristics: ability to use low-cost catalyst, high temperature exhaust heat for cogeneration application, tolerance to some impurities e.g. CO and sulfur, internal reforming within the cell for reducing equipment cost, etc. For the SOFC system, bioethanol feed is heated up and reformed to hydrogen rich gas by the reformer before being introduced into the fuel cell at the anode side coupled with air feed at the cathode side for producing electricity. To achieve better performance from this process, it is necessary to consider every unit within the SOFC system. These units are investigated through their physical structure design and modification on the basis of worthwhile energy utilization in each unit and suitable energy allocation within the process to target an optimum energy management of the SOFC system. The objective of this chapter is to propose ideas and feasible approaches on how to improve the performance of bioethanol-fuelled SOFC systems by focusing on each essential unit modification in the process. Relevant useful approaches from other scientific literature reviews are included. The pros and cons in each proposed method are also discussed. Bioethanol pretreatment unit regarded as a significant unit compared to the other units for the process development is of particular focus in this chapter. The progressive work of our research on the efficiency improvement of the SOFC system with analytically appropriate selection of bioethanol pretreatment unit is presented. The simulation studies were conducted via experimental-verified SOFC model to predict the results under a frame of model assumptions. Performance assessment of the system in any scenario cases held the criteria of no external energy demand condition or $Q_{\text{net}} = 0$ to compare and identify the optimal operating conditions among those of bioethanol pretreatment units. The simulation results could initially guide the right pathway for practical industrial applications.

2. Bioethanol

Among various biomass-based fuel types such as bioethanol, biodiesel, bioglycerol, and biogas, bioethanol is considered a promising renewable energy compared to other biofuels. As shown in Table 1, the maximum amount of work from the fuel cell integrated with fuel processor system in comparison with five renewable fuels including *n*-octane represented as a gasoline characteristic are presented (Delsman et al., 2006). It was indicated that ethanol can offer the highest energy output (based on MJ/mol fuel) among the other renewable fuels (methanol, methane, ammonia, and hydrogen) except for *n*-octane. Furthermore, there are other outstanding advantages of bioethanol given by the following reasons. The production technologies of bioethanol are more mature and cheaper than those of biomethanol (Xuan et al., 2009). Biodiesel which is a popular alternative energy used in vehicle engines can be derived from ethanol (or purified bioethanol) reacted with vegetable oil via transesterification reaction. Biogas is a widely-used renewable power source because of many available feedstocks. It can be produced from several organic wastes by anaerobic biological fermentation. Consequently, it seems to be a promising renewable fuel but biogas mainly consists of methane and CO₂. Both gases have serious negative environmental impacts especially from methane. Methane can remain in atmosphere for 9-15 years and retains heat radiation of 20 times higher than CO₂ (U.S. Environmental Protection Agency). Furthermore, if the biogas is produced from non-agricultural wastes, e.g. cow and pig manure, it would bring this biogas production diverted from carbon-closed cycle. Hence, biogas should be produced and utilized in an effective way. Bioethanol production is mostly derived from biological fermentation using agro-based raw materials such as sucrose-

containing crops, starchy materials, lignocellulosic biomass and agro-waste (Carlos & Oscar, 2007). In addition, the latest research reports that animal manure waste, waste paper, citrus peel waste, and municipal solid waste can be used as feedstock of bioethanol production by using saccharification and fermentation processes (Lal, 2008; Foyle et al., 2007; Wilkins et al., 2007).

Fuel	Maximum amount of work		
	MJ/mol Fuel	MJ/mol C in Fuel	MJ/mol H ₂ via reforming
Methanol	-0.69	-0.69	-0.23
Ethanol	-1.31	-0.65	-0.22
<i>n</i> -Octane	-5.23	-0.65	-0.21
Ammonia	-0.33		-0.22
Methane	-0.8	-0.80	-0.20
Hydrogen	-0.23		-0.23

Table 1. Maximum amount of work for the conversion of fuels to electricity calculated at 298 K and 1 bar (Source: Delsman et al., 2006)

However, bioethanol fermentation is a complicated process. The overall process is schematically shown in Figure 1. It requires many steps of biomass feed conditioning or pretreatment which can be mainly divided into four techniques as follows (Magnusson, 2006):

- Mechanical techniques: biomass is milled or ground to reduce sizes of material,
- Chemical techniques: biomasses e.g. hemicelluloses and lignin are swelled or dissolved by acids, bases, and solvents to transform into pre-hydrolysis form,
- Mechanical-chemical techniques: a combined mechanical and chemical technique e.g. heat pretreatment with high-pressure of steam, and
- Biological techniques: biomass is digested by enzymes or micro-organisms.

Thereafter, the pre-conditioned biomass is biologically transformed into ethanol. This procedure is a key step to be accounted for increasing bioethanol productivity. The basic concept of reactor design is applied with enzymatic fermentation technology. Starting from a simple batch reactor, this is close to organic culture system environment but a batch culture envisages the limitation of enlarging bioethanol production scale. Afterward, semi-batch reactors combining the benefits of batch and continuous reactors are employed. It can offer a long lifetime of cell culture, higher ethanol and cell concentration (Frison & Memmert, 2002). Finally, a continuous flow reactor is applied with cell recycle operation to serve more bioethanol productivity requirement. Influent stream containing substrate, nutrients and culture medium is fed to an agitated bioreactor. The product is removed from the fermenter but the residues (cells and nutrients) are collected and recycled to the vessel. In addition, the concept of process integration is introduced to the bioethanol production application such as Separate Hydrolysis and Fermentation (SHF), Simultaneous Saccharification and Fermentation (SSF) and Direct Microbial Conversion (DMC) (Balat, 2011). In the last step, the obtained dilute ethanol is then purified to gain a desired ethanol concentration. These difficult procedures need to be further developed to reduce the complexity and enable the process to compete with the cheaper oil-derived fuel production.

Many researchers attempt to develop such a biotechnical bioethanol production to be cost-effective. Effective tools for the process evaluation such as thermo-economic, environmental indexes, process optimization and etc. are used to analyze the bioethanol production process as performance indicators to assist in the task of process design. Process integration is regarded as a significant approach since several production procedures are combined into a single unit. It can reduce production costs and provide a more intensive process. For example, the fermentation process integrated with membrane distillation (Gryta, 2001) involved the combination of tubular bioreactor and membrane distillation to synergistically enhance the yield of bioethanol without several units being required as for other common processes. A role of membrane distillation is to remove byproduct from the fermentation broth in bioreactor that can simultaneously forward glucose conversion to gain more ethanol. The objective of process integration is to have the energy requirement in procedures of bioethanol production to be less than the energy obtained from the bioethanol exploitation to utilize bioethanol effectively.

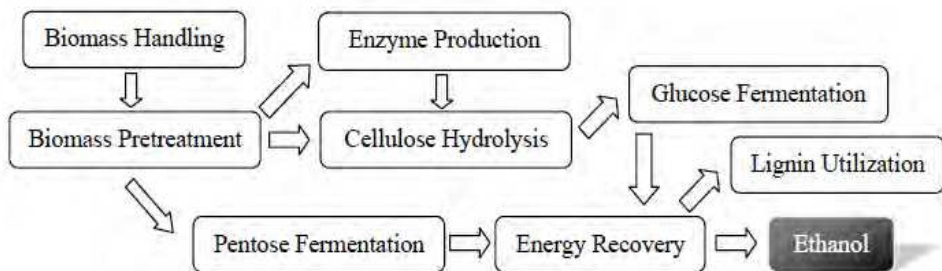


Fig. 1. Schematic diagram of bioethanol production process (Source: U.S. Department of Energy)

Bioethanol can be purified to anhydrous ethanol which is a useful chemical for various applications such as organic solvent, chemical reagent, reactant for biodiesel production, pharmaceutical formations, plastics, polishes and cosmetics industries (Kumar et al., 2010). However, in this chapter, the use of bioethanol is particularly focused on a role of renewable fuel. Application of bioethanol in term of fuel can be mainly divided by two directions:

- Direct combustion to gain thermal energy
- Reforming into hydrogen for clean energy production in a fuel cell

For conventional direct combustion, it seems to be less complicated but the fuel is utilized in an ineffective way because thermal energy accumulated in bioethanol is obviously lower than fossil fuel as shown in Table 2.

Fuel	Density (kg/l)	Caloric value at 20°C (MJ/kg)	Caloric value (MJ/l)	Octane-number (RON)	Fuel-equivalence (l)
Petrol	0.76	42.7	32.45	92	1
Bioethanol	0.79	26.8	21.17	>100	0.65

Table 2. Properties of bioethanol in comparison with petrol (Source: Paul & Kemnitz, 2006)

Moreover, since water is the main constituent in bioethanol, the direct combustion of bioethanol is not possible. However, there is another effective way which is the conversion of bioethanol fuel into hydrogen rich gas. As presented in Table 3, the heating value of hydrogen is higher than that of ethanol (4.47 times). Therefore, the bioethanol reforming process for producing hydrogen is a promising pathway in term of upgrading fuel quality which can offer a higher performance for the SOFC system even in the combustion heat engine while the bioethanol fuel utilization can be conducted in an efficient way.

Fuel	Lower Heating Value (25 °C and 1atm)
Hydrogen	119.93 kJ/g
Methane	50.02 kJ/g
Gasoline	44.5 kJ/g
Diesel	42.5 kJ/g
Ethanol	26.82 kJ/g
Methanol	18.05 kJ/g

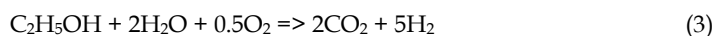
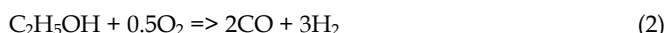
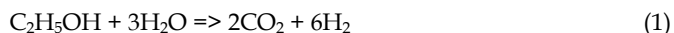
Table 3. Heating values of commonly-used fuels in comparison

Typically, there are three main reforming reactions for hydrogen production as described below:

- Steam reforming
- Partial oxidation
- Autothermal reforming

Selection of an appropriate operation mode depends on the individual objective. Ethanol steam reforming (ESR) (Reaction (1)) is a suitable choice for the SOFC system because this reaction can produce hydrogen at high yield. Although ESR consumes a great amount of heat due to its high endothermicity, heat released from the fuel cell is enough to supply the heat demand for the reaction. For the ethanol partial oxidation (EPOX) (Reaction (2)), it is appropriate for the process required less complexity and integration design. Since EPOX requires the fuel to be partly combusted with air and releases thermal energy as an exothermic reaction, heat and steam supply are not required (Vourliotakis et al., 2009). Nonetheless, this reaction is less selective to hydrogen compared to the former reaction.

Autothermal reforming (ATR) is a combination of the previous two reactions in order to improve the hydrogen selectivity with minimum heat supply. The steam to carbon molar ratio and air to carbon molar ratio are significant parameters to adjust the system to operate close to thermal neutral condition from the exothermic partial oxidation and endothermic steam reforming. Generally, this reaction formula is defined as Reaction (3) with the standard exothermic heat $\Delta H_{298K} = 50$ kJ/mol (Deluga et al., 2004). There is a scientific literature (Liguras et al., 2003) reporting the stoichiometric ratio of H₂O and O₂ of 1.78 and 0.61, respectively per mol of ethanol can carry out thermal neutrality as shown in Reaction (4) but the yield of hydrogen becomes a little lower.





3. Solid oxide fuel cell system fuelled by bioethanol

As mentioned earlier, utilization of bioethanol by being converted into H_2 for electrical power generation via SOFC is recognised. Thus, this section describes the fundamental process of an SOFC system fuelled by bioethanol and the criteria used to define the performance evaluation indicators of this SOFC system as follows:

3.1 Process description

The bioethanol-fuelled SOFC system basically consists of a bioethanol pretreatment unit, preheaters, reformer, fuel cell, and afterburner as illustrated in Figure 2. Bioethanol is purified in the pretreatment unit to achieve a specified ethanol concentration (25mol% ethanol, a suitable stoichiometric ratio for the ethanol steam reforming reaction in Reaction (1)). Then, the steam with a desired ethanol is fed to an external reformer operated under thermodynamic equilibrium condition. Ethanol steam reforming is selected for converting the raw materials into hydrogen rich gas. The reaction is assumed to occur isothermally in the reformer. Finally, the reformed influent stream is fed to the SOFC's anode chamber together with excess air (5 times) preheated and fed to the cathode chamber to produce electricity and thermal energy. The effluent steam containing residual fuel released from the fuel cell is combusted in the afterburner and heat from the fuel combustion is recovered to supply all the heat-demanding units i.e. preheaters, purification unit, and reformer. The final temperature of exhaust gas emitted to atmosphere is specified at 403K (Jamsak et al., 2007). The performance of the SOFC system can be simulated using Aspen Plus software.

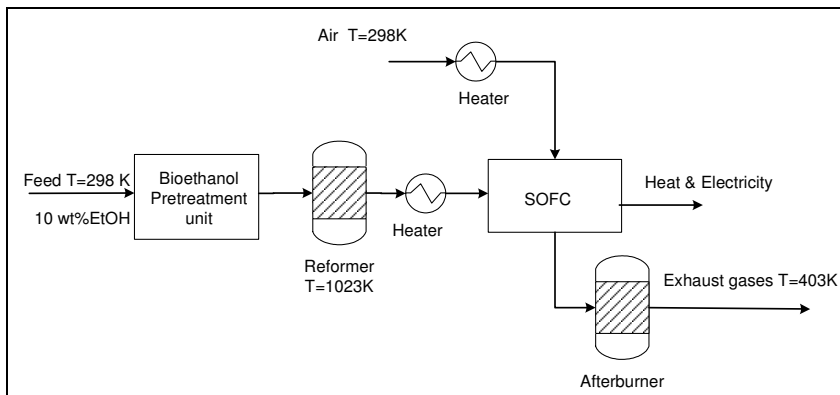


Fig. 2. Basic process diagram of bioethanol-fuelled SOFC system

3.2 Mathematical model

The SOFC model was adapted from the prior literature of Piroonlerkgul et al., 2008 to study the performance of SOFC system. From this model, a constant operating voltage along the cell length and isothermal condition were assumed. Only hydrogen oxidation was considered to react electrochemically within the fuel cell. Oxygen ion electrolyte type was chosen for the SOFC and its electrochemical reactions are described below:



The validation of this model was in a good agreement with experimental results (Zhao et al., 2005; Tao et al., 2005) at high hydrogen contents (hydrogen mole fraction = 0.97) and (Petruzzi et al., 2003) at low hydrogen contents (hydrogen mole fraction = 0.26). The materials used in the SOFC stack were YSZ, Ni-YSZ and LSM-YSZ for electrolyte, anode and cathode, respectively.

3.2.1 Electrochemical model

3.2.1.1 Open circuit voltage

The open circuit voltage (E) is formulated by the Nernst equation given in Eq. (7)

$$E = E_0 + \frac{RT}{F} \ln \left(\frac{P_{\text{H}_2} P_{\text{O}_2}^{1/2}}{P_{\text{H}_2\text{O}}} \right) \quad (7)$$

where F is Faraday constant (C mol^{-1}) and P_i is a partial pressure of component i .

The actual operating voltage (V) is less than the open circuit voltage (E) due to the presence of various polarizations. Three types of polarization are considered in this model: Ohmic, Activation, and Concentration polarizations as below:

$$V = E - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}} \quad (8)$$

3.2.1.2 Polarizations

3.2.1.2.1 Ohmic polarization

This ohmic polarization involves the resistance of both ions flowing in the electrolyte and electrons flowing through the electrodes. This resistance loss is regarded as a major loss in the SOFC stack given as:

$$\eta_{\text{ohmic}} = 2.99 \times 10^{-11} i L \exp \left(\frac{10300}{T} \right) \quad (9)$$

where i is current density and L is thickness of anode electrode

3.2.1.2.2 Activation polarization

Activation polarization is caused by the loss of electrochemical reaction rate at the electrodes. An operation of SOFC at high temperature can reduce this polarization as the rate-determining step becomes faster. Normally, activation polarization region occurs in the low current density range. This polarization is defined by the Butler-Volmer equation.

$$i = i_0 \left[\exp \left(\frac{\alpha z F \eta_{\text{act}}}{RT} \right) - \exp \left(- \frac{(1-\alpha) z F \eta_{\text{act}}}{RT} \right) \right] \quad (10)$$

The value of a and z were specified as 0.5 and 2 (Chan et al., 2001), respectively. Accordingly, the activation polarization at the anode and cathode sides can be arranged into another form as:

$$\eta_{\text{act},j} = \frac{RT}{F} \sinh^{-1} \left(\frac{i}{2i_{0,j}} \right) \quad (11)$$

where j = anode, cathode

The exchange current density ($i_{0,j}$) for both the anode and cathode sides are expressed as follows:

$$i_{0,a} = \gamma_a \left(\frac{P_{\text{H}_2}}{P_{\text{ref}}} \right) \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{ref}}} \right) \exp \left(-\frac{E_{\text{act},a}}{RT} \right) \quad (12)$$

$$i_{0,c} = \gamma_c \left(\frac{P_{\text{O}_2}}{P_{\text{ref}}} \right)^{0.25} \exp \left(-\frac{E_{\text{act},c}}{RT} \right) \quad (13)$$

where γ_a and γ_c are pre-exponential factors for anode and cathode current densities, respectively.

3.2.1.2.3 Concentration polarization

This polarization arises from the difference in gas partial pressures in the porous electrode region due to slow mass transport. It can be estimated by Eqs. (14) and (15) for the anode and cathode sides, respectively.

$$\eta_{\text{conc},a} = \frac{RT}{2F} \ln \left[\frac{\left(1 + (RT/2F)(l_a/D_{a(\text{eff})}P_{\text{H}_2\text{O}}^I i) \right)}{\left(1 - (RT/2F)(l_a/D_{a(\text{eff})}P_{\text{H}_2}^I i) \right)} \right] \quad (14)$$

$$\eta_{\text{conc},c} = \frac{RT}{4F} \ln \left[\frac{P_{\text{O}_2}^I}{(p_c/\delta_{\text{O}_2}) - ((p_c/\delta_{\text{O}_2}) - p_{\text{O}_2}^I) \exp \left[(RT/4F)(\delta_{\text{O}_2} l_c / D_{c(\text{eff})} p_c) i \right]} \right] \quad (15)$$

where l_a and l_c are thicknesses of anode and cathode electrodes, respectively, while δ_{O_2} , $D_{a(\text{eff})}$ and $D_{c(\text{eff})}$ are given by:

$$\delta_{\text{O}_2} = \frac{D_{\text{O}_2,k(\text{eff})}}{D_{\text{O}_2,k(\text{eff})} + D_{\text{O}_2-\text{N}_2(\text{eff})}} \quad (16)$$

$$D_{a(\text{eff})} = \left(\frac{P_{\text{H}_2\text{O}}}{P_a} \right) D_{\text{H}_2(\text{eff})} + \left(\frac{P_{\text{H}_2}}{P_a} \right) D_{\text{H}_2\text{O}(\text{eff})} \quad (17)$$

$$D_{c(\text{eff})} = \frac{\xi}{n} \left(\frac{1}{D_{\text{O}_2,k}} + \frac{1}{D_{\text{O}_2-\text{N}_2}} \right) \quad (18)$$

$$\frac{1}{D_{\text{H}_2(\text{eff})}} = \frac{\xi}{n} \left(\frac{1}{D_{\text{H}_2,k}} + \frac{1}{D_{\text{H}_2-\text{H}_2\text{O}}} \right) \quad (19)$$

$$\frac{1}{D_{\text{H}_2\text{O}}(\text{eff})} = \frac{\xi}{n} \left(\frac{1}{D_{\text{H}_2\text{O},k}} + \frac{1}{D_{\text{H}_2-\text{H}_2\text{O}}} \right) \quad (20)$$

The relationship between the effective diffusion parameter (D_{eff}) and ordinary diffusion parameter (D) can be described by:

$$D_{\text{(eff)}} = \frac{n}{\xi} D \quad (21)$$

where n is electrode porosity and ξ is electrode tortuosity. Assuming straight and round pores, the Knudsen diffusion parameter can be calculated by:

$$D_{A,k} = 9700 \sqrt{\frac{T}{M_A}} \quad (22)$$

The binary ordinary diffusion parameter in a gas phase can be calculated using the Chapman-Enskog theory of prediction as below:

$$D_{A-B} = 1.8583 \times 10^{-3} \left(\frac{T^{3/2} ((1/M_A) + (1/M_B))^{1/2}}{P \sigma_{AB}^2 \Omega_D} \right) \quad (23)$$

where σ_{AB} the characteristic length, M_i is molecular weight of gas i , and Ω_D is the collision integral. These parameters are given by:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \quad (24)$$

$$\Omega_D = \frac{A}{T_k^B} + \frac{C}{\exp(DT_k)} + \frac{E}{\exp(FT_k)} + \frac{G}{\exp(HT_k)} \quad (25)$$

where the constants A to H are $A = 1.06036$, $B = 0.15610$, $C = 0.19300$, $D = 0.47635$, $E = 1.03587$, $F = 1.52996$, $G = 1.76474$, $H = 3.89411$.

3.3 Evaluation of process performance

The proposed bioethanol-fuelled SOFC system for electrical power generation needs to be evaluated together with any process design adjustments to obtain optimum performance. A number of criteria can be used to define the performance of the system, e.g. economic, 1st and 2nd laws of thermodynamics, environment, etc. Fundamentally, the overall performance evaluation of an SOFC system is defined in terms of electrical efficiency as below:

$$\eta_{\text{elec,ov}} = \frac{\text{Net electrical power output}}{\text{mol}_{\text{Fuel}} \cdot \text{LHV}_{\text{Fuel}}} \quad (26)$$

The definition of the above equation is energy efficiency based on 1st law of thermodynamics which initially accounts on an ideal energy conservation law. Fuel input term is referred to the lower heating value (LHV). In considering an energy loss from the system which is closer to actual condition, the definition of overall system efficiency is formulated as follows:

$$\eta_{\text{elec,ov}} = \frac{\text{Net electrical power output}}{\text{mol}_{\text{Fuel}} \cdot e_{\text{Fuel}}^{\circ}} \quad (27)$$

This equation is exergy efficiency which further takes the 2nd law of thermodynamic into account stated that entropy loss occurred in the system with highly irreversible process especially combustion process. The fuel input denominator in Eq. (27) is referred to the standard exergetic potential of fuel. In addition, the analysis in term of exergy can determine the location, source, and amount of actual thermodynamic inefficiencies in each unit. Profound understanding can be perceived from this analysis for solving the process problem correctly.

The criterion mainly considered in this chapter is no external energy demand condition. In the SOFC system, there are units having the roles of both energy consumption and generation. Before investigating and evaluating the system efficiency, energy consumed or generated from the units is allocated within the system until the overall system is under self-sufficient energy condition or $Q_{\text{net}} = 0$ as follows:

$$Q_{\text{net}} = Q_{\text{generation}} - Q_{\text{demand}} = 0 \quad (28)$$

where $Q_{\text{generation}}$ represents the heat from units which can generate thermal energy (SOFC and afterburner) while Q_{demand} expressed as the heat from units which consume heat (bioethanol pretreatment unit, heaters, and reformer). The system operated at such a condition can help allocate energy within the process effectively. The exhaust gas released to atmosphere is specified at 403 K (Jamsak et al., 2007). The consideration of $Q_{\text{net}} = 0$ associated with the process evaluation has led to the modified efficiency definition:

$$\eta_{\text{elec,ov}} = \frac{\text{Net electrical power output}}{\text{mol}_{\text{Fuel}} \cdot \text{LHV}_{\text{Fuel}} + \text{external heat demand}} \quad (29)$$

In case of incorporating a heat recovery unit such as combined heat and power (CHP) with the SOFC system, the definition of efficiency is adjusted to:

$$\eta_{\text{elec,ov}} = \frac{\text{Net electrical power output} + \text{exchanged thermal energy}}{\text{mol}_{\text{Fuel}} \cdot \text{LHV}_{\text{Fuel}} + \text{external heat demand}} \quad (30)$$

4. Process modification for improving performance of the SOFC system

The fundamental process of the bioethanol-fuelled SOFC system needs to be further developed to utilize bioethanol effectively and achieve higher electrical efficiency. In this chapter, the performance improvement of SOFC systems under consideration is based on selection for appropriate units. The possible units are structurally modified and evaluated for their energy consumption. The process modification of the SOFC system can be divided by two main scopes including adjusting the fuel cell module and improving the balance of plant.

4.1 Solid Oxide Fuel Cell

Originally, the Solid Oxide Fuel Cell (SOFC) is classified as a high-temperature fuel cell. Due to the demand for high cost materials and fabrication, the intermediate temperature solid

oxide fuel cell was later developed with the research into novel material technology and thin layer techniques applied in electrolyte and electrodes. Regarding the fuel cell geometry design, it is useful to differentiate the scope into macro and micro geometry configurations. The micro geometry covering the structures of anode, electrolyte, and cathode has direct effects on the electrochemical performance of the fuel cell. The heat transfer mechanisms of convection and conduction through heat exchange areas and the mass transport through active surface areas are influenced by the macro geometry (Nagel et al., 2008). Generally, primary structures of SOFC are tubular, planar, and monolithic as shown in Figures (3), (4), and (5), respectively. The SOFC structure of planar design is more compact than the tubular design and also offers higher ratio of power per volume (Pramuanjaroenkij et al., 2008). For the monolithic design, this SOFC design uses the similar concept with shell-and-tube heat exchanger. It combines the tri-layer of anode-electrolyte-cathode into a compact corrugated structure. This design can assist a thermal energy allocation exchanged between the flow channels and size of the fuel cell to become more compact with the corrugated self-supporting structure.

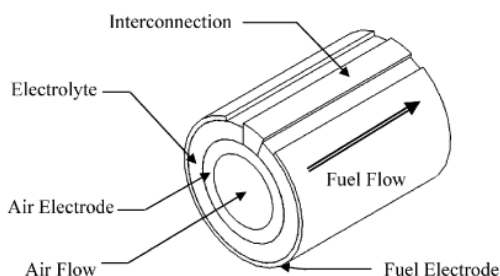


Fig. 3. Schematic of tubular SOFC (Source: Kakac et al., 2007)

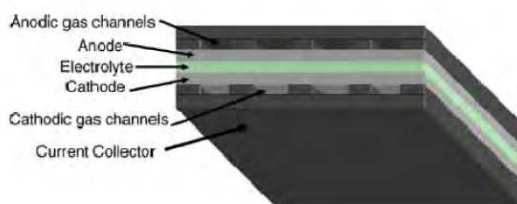


Fig. 4. Schematic of planar SOFC (Source: Bove & Ubertini, 2006)

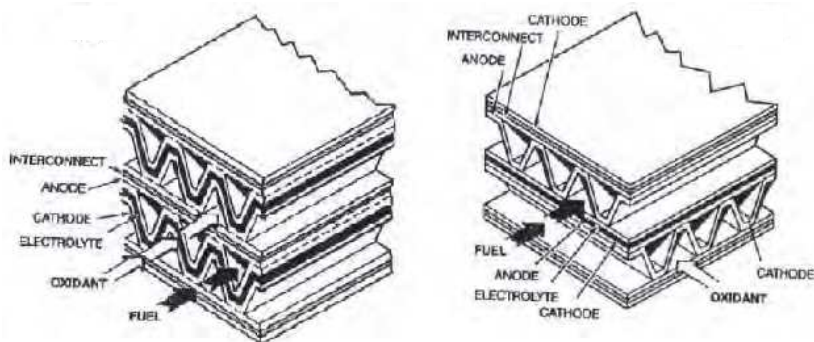


Fig. 5. Schematic of monolithic SOFC; (Left) coflow and (Right) cross flow (Source: Minh, 1993)

4.2 Balance of plant

There are essential units around the fuel cell as supporting units for the overall electrical power generation process. These units can be modified to utilize energy within their system units suitably. Sections in the balance of plant which are potential in improving the efficiency of SOFC system are described as follows:

4.2.1 Bioethanol pretreatment section

This section has a key role in improving the efficiency of the SOFC system. Originally, bioethanol has a low concentration in a range of 1-7 mol% (Shell et al., 2004; Cardona Alzate & Sanchez Toro, 2006; Roger et al., 1980; Buchholz et al., 1987). In our studies, 10wt% (4.16 mol%) ethanol was specified to represent the range of actual bioethanol concentration. These bioethanol compositions are unsuitable for feeding into the reformer operating under ethanol steam reforming reaction to produce hydrogen because of high water content. Unnecessary thermal energy is required to heat up surplus water within the reformer and the sizes of reformer are larger than necessary. Hence, the bioethanol pretreatment unit plays an important part to purify bioethanol feed into a desired concentration of 25mol% ethanol (46wt% ethanol). A selection of appropriate purification unit for bioethanol conditioning must consider an effective separation with low energy consumption to offer a better performance of the system. In our research (Jamsak et al., 2007), we started with a conventional distillation column used in the bioethanol-fuelled SOFC system as illustrated in Figure 6.

A distillation column is commonly recognised as a high energy consumption unit, but the SOFC released a large amount of exothermic heat. Therefore, it is feasible to apply this unit as a bioethanol pretreatment unit. The results from our simulation studies indicated that there were some operating conditions which can run this system under $Q_{net} = 0$. However, the overall electrical efficiency obtained from this system was quite low due to high reboiler heat duty consumption and high amount of heat loss in the condenser. Afterwards, among the promising membrane technologies, pervaporation is considered as a replacement for the former purification unit as shown in Fig 7. By the principle of physical-chemical affinity between the membrane material and species, this unit consumes only heat for vaporizing a preferential substance permeated through the membrane. However, it is noted that a pervaporation depends on a driving force generation device, typically a vacuum pump is used to boost up its separation performance. Therefore, part of the generated electrical energy must be consumed to operate the device.

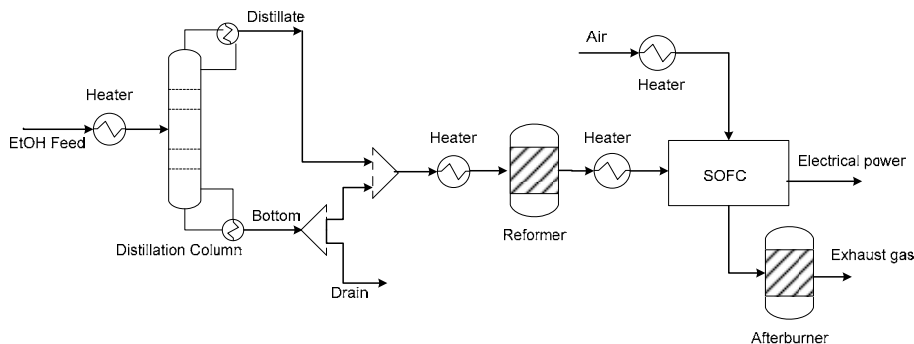


Fig. 6. Process diagram of bioethanol-fuelled SOFC system using a distillation column

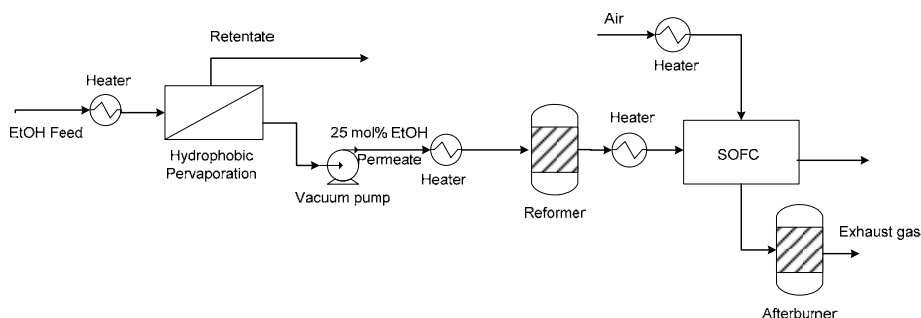


Fig. 7. Process diagram of bioethanol-fuelled SOFC system using a pervaporation

Type of purification process	Energy consumption (MJ/kg ethanol)	Range of concentration (wt%)
Distillation processes		
Low pressure distillation	11.72	6.4-98
Azeotropic distillation		
Pentane	10.05	6.4-99.95
Benzene	15.49	6.4-99.95
Diethyl ether	12.56	6.4-99.95
Extractive distillation		
Gasoline	9.21	6.4-99.95
Ethylene glycol	18.84	6.4-99.95
Extractive distillation with salt		
Calcium chloride	5.02	7.5-99
Potassium acetate	9.27	60
Non-distillation processes		
Solvent extraction	6.28	10-98
Pervaporation	4.61	8-99.5

Table 4. Energy consumption for anhydrous ethanol production from various purification processes (Source: Black, 1980; Jaques et al., 1972; Hala, 1969; Barba et al., 1985; Ligerio and Ravagnani, 2003)

However, a pervaporation is still regarded as being the lowest energy consumption unit among the other purification units as shown in Table 4. (Reviewed by Kumar et al., 2010) that gives an example of using various purification processes for anhydrous ethanol production. To emphasize their mentioned data, the simulation results from our studies (Choedkiatsakul et al., 2011) showed the performance of bioethanol-fuelled SOFC system in comparison between two pretreatments; using distillation and pervaporation units. On the basis of purification process operated at 348K, Table 5 presents the classification of energy term in each unit for both purification processes. Although a pervaporation consumed an electrical energy within the unit, it offers an overall electrical efficiency (42%) superior to that of distillation column (34%). However, a hydrophobic membrane material used in the pervaporation required a high ethanol separation factor property as illustrated in Figure 8 but it may be unavailable in real membrane materials.

Energy distribution	Purification process configuration	
	Pervaporation	Distillation Column
Heat (MW)		
Bioethanol pretreatment unit	2,301	3,580
Reformer	417	421
Air preheater	22,575	23,892
Afterburner	25,293	27,893
Electrical power (MW)		
Bioethanol pretreatment unit	453	0
Electrical production	4,920	3,701
Net electrical energy	4,467	3,701
Fuel utilization (%)	92	68
Overall electrical efficiency (%)	42	34

Table 5. Performance characteristics in comparison between two different purification units based on $Q_{\text{net}} = 0$, ethanol recovery ($R_{\text{EtOH}} = 80\%$), $V = 0.7$ V, and $T_{\text{SOFC}} = 1073$ K (Source: Choedkiatsakul et al., 2011)

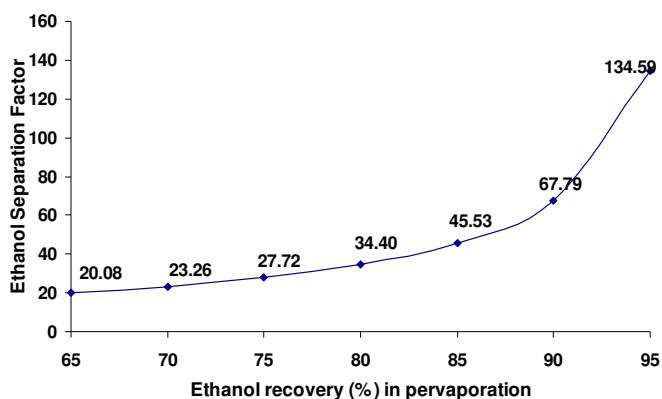


Fig. 8. Effect of ethanol recovery in pervaporation on the required ethanol separation factor of hydrophobic membrane

Consequently, as schematically shown in Figure 9, this problem was solved by having a vapor permeation device installed after a pervaporation (Sukwattanaaroon et al., 2011) to improve ethanol separation performance, an important part of the SOFC system,. The permeate stream of a pervaporation in vapor phase which can be directly fed to a vapor permeator without preheating is a benefit of this technique. From our investigations based on $Q_{net} = 0$, an available hydrophilic membrane of high water separation factor is a suitable choice to be used in a vapor permeation unit. The performance of SOFC system using this proposed purification process obviously overcomes the other two cases as shown in Figure 10.

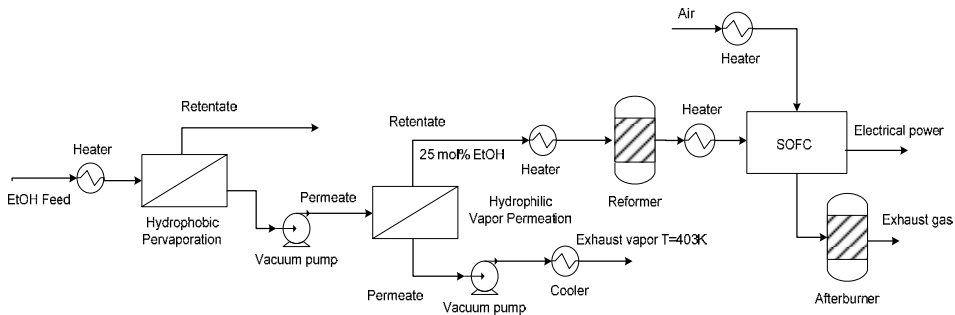


Fig. 9. Process diagram of bioethanol-fuelled SOFC system using a hybrid pervaporation/vapor permeation process

The overall electrical efficiency can be ranked as: Integrated vapour permeation/pervaporation (45.46%) > pervaporation (36.46%) > distillation column (22.53%), respectively.

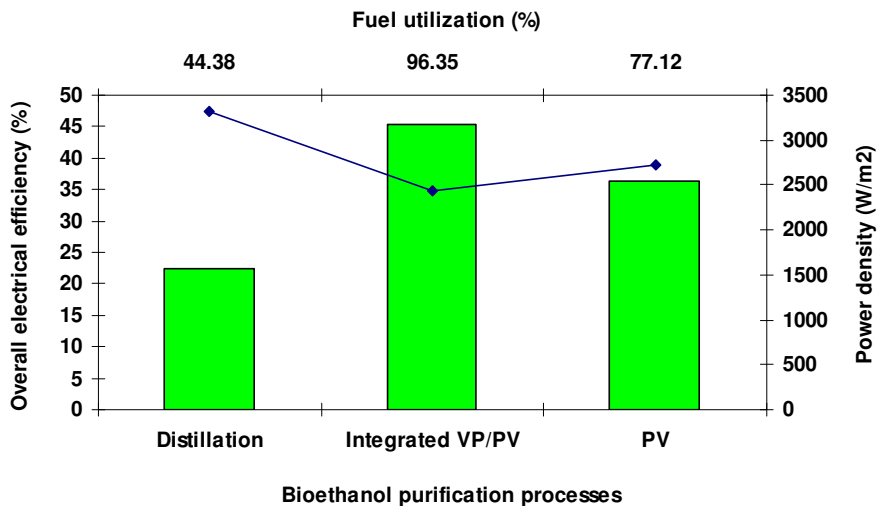


Fig. 10. Performance comparison of SOFC system with various purification processes based on self-sufficient condition ($Q_{net} = 0$, $R_{EtOH} = 75\%$, $V=0.75V$, $T_{SOFC} = 1073K$)

4.2.2 Fuel processing section

Bioethanol was reformed into hydrogen rich gas through a reformer unit which was under the fuel processing section. High yield of desired product and a proper energy management are required for a fuel processor. Structural design of fuel processor is mostly developed to enhance high active surface-to-volume ratio with well-transferred heat. A monolithic reformer is one type of fuel processor design used to increase an active surface area but the compact size of reformer is maintained by designing highly interconnected repeating channels like a honeycomb. The pressure drop along each channel becomes lower. In addition, the monolithic design is resistant to vibration and is stable (Xuan et al., 2009). There is a limit of the temperature control because of its structural design. Nevertheless, heat transfer within the monolithic reformer can be improved by using metallic-typed material as illustrated in Figure 11. Membrane technology is applied to improve the fuel conversion unit which rely on a process integration principle commonly known as membrane reactor. However, Mendes et al., 2010, studied the energy efficiency of the polymer electrolyte membrane fuel cell (PEMFC) system in comparison between a conventional reactor and a membrane reactor operating with ethanol steam reforming. In the case of a conventional reactor, it consists of an ethanol reformer and two water gas shift reactors operating at high and low temperatures, respectively. For a membrane reactor, the multi-tubular module using thin Pd-Ag tubes was employed. The simulation results showed that membrane reactor configuration offers slightly increase of energy efficiency (30%) compared with the conventional reactor (27%) for overall process evaluation. This seems to be impractical because using a membrane-integrated fuel processor requires not only an expensive metal membrane fabrication but also results in short life time due to its low temperature resistance.

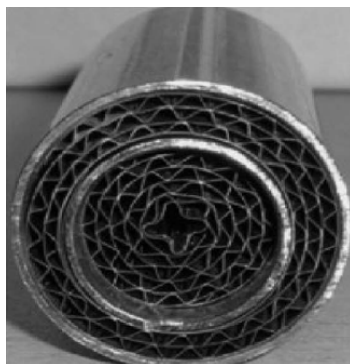


Fig. 11. Metallic-made monolithic reactor (Source: Mei et al., 2007)

Internal reforming is another concept of heat allocation techniques similar to process integration can achieve a better efficiency for the SOFC system and also reduce an external reformer cost. A fuel processing section was incorporated with the fuel cell typically placed at an anode side. Heat demand for the endothermic fuel reforming was supplied by the exothermic heat released from the electrochemical reaction of the fuel cell. The operations of internal reforming are classified into two types depending on the level of contact partition between reformer and anode electrode namely; indirect and direct internal reforming as shown in Figure 12.

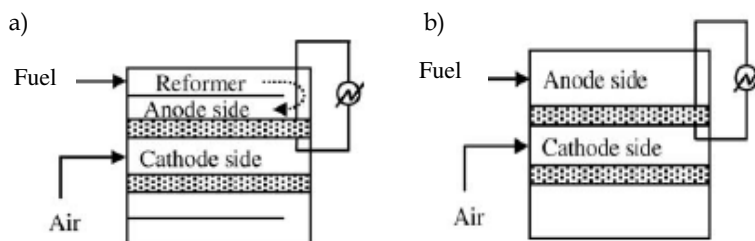


Fig. 12. Type of internal reforming in SOFC: a) Indirect internal reforming, b) Direct internal reforming

Regarding the internal structure of both types of SOFC in Figure 12, direct internal reforming SOFC (DIR-SOFC) can be superior in term of thermal allocation than indirect internal reforming SOFC (IIR-SOFC) owing to its greater contact area of anode electrode. Accordingly, DIR-SOFC can offer a higher overall efficiency. However, by using this operation mode, a carbon formation may occur at on the anode. In our previous work, Assabumrungrat et al., 2004, have investigated the thermodynamic analysis to determine suitable conditions for operating DIR-SOFC fuelled by ethanol to avoid the boundary of carbon formation. From the theoretical calculation results, it is initially suggested that an increase of the H_2O /Ethanol ratio can prevent the carbon formation since adequate water supply leads to a formation of CO_2 rather than CO which is converted to carbon via the Boudard reaction. The oxygen-conducting electrolyte type has lower tendency to form carbon deposition than hydrogen-conducting electrolyte type because the steam product of the first type occurs at the anode side which is the location of fuel processing and thus the additional steam can increase the H_2O /Ethanol ratio in the fuel reforming region.

4.2.3 Heat recovery section

In the SOFC system, after a hydrogen rich gas stream reacted within an SOFC unit under the hydrogen oxidation reaction, an exhaust gas stream containing residual fuel such as H_2 , C_2H_5OH , and CO is introduced to combust in the afterburner unit to recover heat for a supply to other heat-demanding units. This brings the system to be more effective heat management and leads to higher system efficiency. There are several methods for recapturing exhaust heat under the frame of combined heat and power (CHP) principle including the use of extra power generation unit (e.g. steam and gas turbines) and heat recovery unit (e.g. recuperator, steam boiler, and heat exchanger network). Selimovic et al., 2002 proposed that networked SOFC stacks incorporated with gas turbine be used to further produce electricity from an exhaust gas combustion stream. It is known that a gas turbine is classified as a low efficiency mechanical power device as well as an entropy lost afterburner. The simulation results showed that the scenario case which allocated fuel utilization portion to the group of afterburner and gas turbine yields higher system efficiency than the scenario case of preferentially allocated fuel utilization portion to the fuel cell. Therefore, it is a good attempt to operate the fuel cell at full performance with high fuel utilization to avoid the step of fuel combustion in the system.

Our previous work (Jamsak et al., 2009) has proposed the MER (maximum energy recovery) under the concept of cogeneration to improve the performance of bioethanol-fuelled SOFC system integrated with distillation column presented in the previous section. Heat transfer

arrangement covering useful heat sources i.e. condenser duty, hot water from the bottom of the distillation column, and hot air of cathode recirculation is considered in this study. In the earlier study, system configurations are divided into 5 cases as follows:

- Base case (No-HX)
- Heat exchanged between the condenser and bioethanol feed stream (CondBio)
- Heat exchanged between hot water from the bottom of column and bioethanol inlet stream (HW-Cond)
- Heat exchanged between the condenser and air inlet stream (Cond-Air)
- Hot air cathode recirculation (CathRec)

All the system configuration studies are illustrated in Figure 13. The basic heat exchanger network was employed in all cases and the results are shown in Table 6.

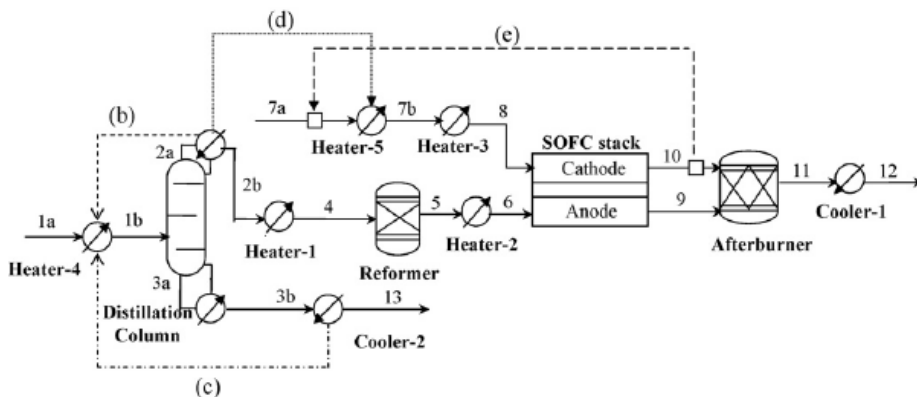


Fig. 13. Process diagram of SOFC system integrated with distillation column: a) No-HX, b) CondBio, c) HW-Cond, d) Cond-Air, and e) CathRec (Source: Jamsak et al., 2009)

Scenario case study	Overall electrical efficiency (%)	CHP efficiency (%)
No-HX	15.79	76.45
CondBio	16.26	78.73
HW-Bio	16.21	78.48
Cond-Air	16.95	81.74
CathRec	21.67	79.87
CondBio-CathRec	22.53	74.71

Table 6. Performance of SOFC system integrated with distillation column with different configurations (Source: Jamsak et al., 2009)

With regard to preheating the bioethanol inlet stream, CondBio can offer both overall electrical efficiency and CHP efficiency higher than those of HW-Bio. Thus, CondBio case is chosen for preheating bioethanol inlet stream. For preheating the air inlet stream, there are two options: Cond-Air and CathRec. Since the condenser has already been used for a bioethanol inlet stream, CathRec has to be selected although its CHP efficiency is slightly less than that of Cond-Air. Afterwards, the CondBio and CathRec are then combined to become a new case: CondBio-CathRec, and its result as shown in Table 6 provides the

highest overall electrical efficiency. In addition, this case is further developed by using MER network design. The performance achieved from this design gives 40.8% and 54.3% for overall electrical efficiency and CHP efficiency with the base conditions (25mol%ethanol, ethanol recovery = 80%, operating voltage = 0.7V, fuel utilization = 80%, and operating temperature = 1200K), respectively, compared to the previous SOFC system integrated with distillation column without MER design which gives 33.3% for overall electrical efficiency .

5. Conclusions

This chapter has presented the important use of bioethanol applied as a renewable fuel for producing electricity by Solid Oxide Fuel Cell (SOFC) system. Bioethanol must be upgraded by purifying and reforming into hydrogen rich gas which can be further applied as a clean fuel for direct combustion or electrical power generation by the fuel cell. The later option is chosen as it was realized that bioethanol was worthily utilized in an effective way. The performance development of this system was proposed through our research and the other related scientific literature reviews. Macro level of physical structure design is taken into account for initially guiding a right path for system improvement. Process modification of the system is divided into two main scopes; SOFC and Balance of Plant. The Balance of Plant as a supporting part consists of fuel processing section, bioethanol pre-treatment section, and heat recovery section. All of these are necessary in the concept of process integration and cogeneration to reduce high energy consumption and difficulties within each unit. Bioethanol pretreatment section which is an essential part has been the focus in this chapter. Our evolution of the purification process improvement was proposed. Membrane technology is a promising alternative to be applied in this section and the outcome of SOFC system performance after using this technology is in good agreement with primary mathematical simulation and the criterion of no external energy demand condition. However, an economic assessment and practical experiment in term of investigating working life time should be taken into account for the further study.

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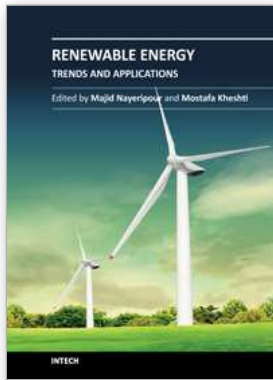
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