CHAPTER IV

MODELING

This chapter describes all related simulation models and procedures of calculation including SOFC system and bioethanol pretreatment processes. VBA (Visual Basic for Application) on Excel spreadsheet was used for simulating the SOFC system to assess overall performance while the purification units i.e. pervaporation and vapor permeation were investigated using preliminary calculations on Excel spreadsheet. The distillation column was simulated using Aspen Plus to evaluate its performance.

4.1 Bioethanol Pretreatment Process

Bioethanol, a part of several renewable resources, was selected to be a fuel feed for SOFC system. As mentioned earlier, bioethanol derived from fermentation broth contains mainly water. In this research, bioethanol feed is assumed to consist of only ethanol and water. It is specified at 10 wt% or 4.16 mol% ethanol at ambient condition in accordance with a range of actual bioethanol containing about 5-12 wt% ethanol (S. Ramaswamy et al., 2008) before being fed into a pretreatment unit as follows:

4.1.1 Preliminary Calculations of Pervaporation and Vapor Permeation

Performance assessment of pervaporation and vapor permeation is conducted under a basic calculation to present the primary results. Various parameters and their criteria were considered based on theory. To reduce the complexity, this calculation defines the ethanol recovery parameter representing the influence from other significant parameters on membrane separation as shown in Eq. (4.1).

$$R_{\mathrm{EtOH}} = \mathrm{f}^{\mathrm{n}}(T_{\mathrm{Feed}}, \text{membrane area, feed composition, permeate side conditions,}\ldots)$$
$$= \frac{y_{p(EtOH)}P}{x_{F(EtOH)}F} \qquad (4.1)$$

The mass balance equations of pervaporation and vapor permeation are determined as

$$F = P + R \tag{4.2}$$

$$x_{F_i}F = y_{P_i}P + x_{R_i}R \tag{4.3}$$

where F is the total feed, P is the permeate stream, R is the retentate stream, while x_i and y_i represent molar fraction of species i of the retentate and permeate, respectively.

The separation factor as a performance indicator of membrane is another parameter to be employed in the calculation incorporated with ethanol recovery as shown below:

$$\propto_{i/j} = \frac{y_i/y_j}{x_i/x_j} \tag{4.4}$$

In this set of equations, the ethanol concentration of 25 mol% is specified at the permeate stream and retentate stream for hydrophobic and hydrophilic membrane types, respectively. Thereafter, the calculated separation factor values in each type are then obtained including the mass flow rate of permeate and retentate streams. For energy calculation, there are different between pervaporation and vapor permeation. In a pervaporation, heat utilized from sensible heat of liquid feed mixture is necessary for vaporizing a preferential component to be permeated through the membrane. However, the temperature drop is neglected to simplify the calculation. According to the pervaporation, the operating temperatures are limited to below 373 K (R. Smith, 2005), this pervaporation module is defined to operate at 348 K under isothermal condition. The total required thermal energy is shown by the following equation:

$$Q = m\int_{T_{in}}^{T_{out}} C_p dT + mL \tag{4.5}$$

For vapor permeation, thermal energy is required only for the first term of Eq. (4.5) since there is no phase change in the separation mechanism. There are many methods for generating a driving force for the membrane separation. A vacuum pump is considered in this study and is installed in a permeate side to drive chemical potential gradient through the pressure difference. The electrical power required for operating the vacuum pump is calculated by using Eqs. (4.6) and (4.7), respectively.

$$T_{out} = T_{in}\left[1 + \frac{1}{\eta_{pump}}\left[\left(\frac{P_{out}}{P_{in}}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]\right] \quad (4.6)$$

$$W_{e,PV} = -m_p \int_{T_{in}}^{T_{out}} C_p dT \quad (4.7)$$

where
$$\gamma = \frac{C_p}{C_p - R} \quad (4.8)$$

The electrical efficiency of a vacuum pump was specified at 75% (T. Kaneko et al., 2006).

4.1.2 Distillation Column

A distillation column which was used as a bioethanol purification unit for the SOFC system in the previous work (Wassana Jamsak et al., 2007) was considered to compare its performance of SOFC system with the proposed purification process-integrated SOFC system of this work under the same conditions to demonstrate its performance improvement. The procedure of bioethanol pretreatment using an ordinary distillation column to obtain a desired concentration is depicted in Figure 4.1.

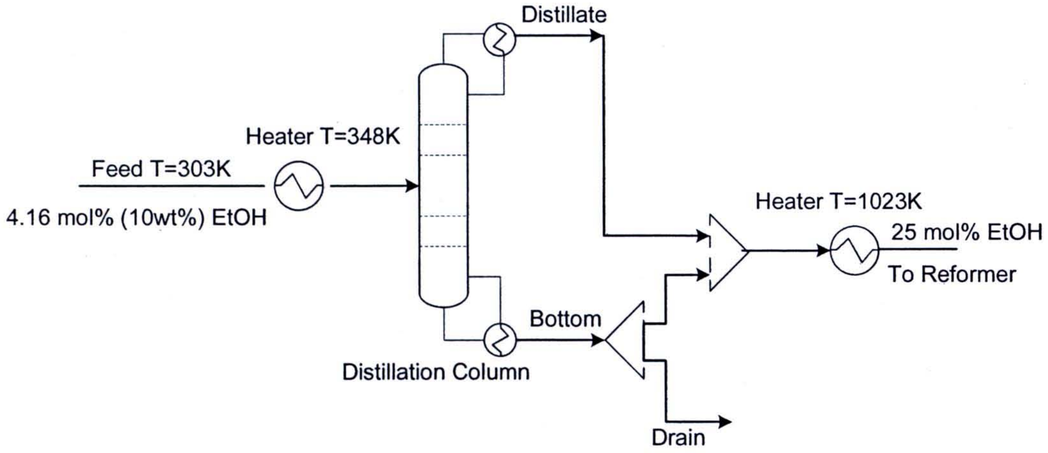

Figure 4.1 The schematic diagram of ordinary distillation column

4.2 SOFC model

The SOFC model was applied from the previous literature (Pakorn Piroonlerkgul et al., 2008) to investigate the overall performance of SOFC system. In 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 module. Oxygen ion electrolyte type was selected for SOFC and its electrochemical reaction occurring as follows:

$$1/2O_2 + 2e^- \rightarrow O^{2-} \tag{4.9}$$

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{4.10}$$

The verification of the model was in good agreement with experimental results of Zhao et al., (2005) and 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 SOFC stack are YSZ, Ni-YSZ and LSM-YSZ for electrolyte, anode and cathode, respectively.

4.2.1 Electrochemical model

4.2.1.1 Open circuit voltage

The open circuit voltage (*E*) is calculated by the Nernst equation as given in Eq. (4.11)

$$E = E_0 + \frac{RT}{F}\ln\left(\frac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2O}}\right) \tag{4.11}$$

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

$$V = E - \eta_{act} - \eta_{ohmic} - \eta_{conc} \tag{4.12}$$

4.2.1.2 Polarizations

- Ohmic polarization

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

$$\eta_{ohmic} = 2.99x10^{-11} iL\exp\left(\frac{10300}{T}\right) \tag{4.13}$$

- 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 locates at low current density range. This polarization is defined by Butler-Volmer equation.

$$i = i_0\left[\exp\left(\frac{\alpha zF\eta_{act}}{RT}\right) - \exp\left(-\frac{(1-\alpha)zF\eta_{act}}{RT}\right)\right] \tag{4.14}$$

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

$$\eta_{act,j} = \frac{RT}{F}\sinh^{-1}\left(\frac{i}{2i_{0,j}}\right) \quad , \mathrm{j = anode, cathode} \tag{4.15}$$

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

$$i_{o,a} = \gamma_a\left(\frac{P_{H_2}}{P_{ref}}\right)\left(\frac{P_{H_2O}}{P_{ref}}\right)\exp\left(-\frac{E_{act,a}}{RT}\right) \tag{4.16}$$

$$i_{o,c} = \gamma_c \left(\frac{P_{O_2}}{P_{ref}} \right)^{0.25} \exp\left(-\frac{E_{act,c}}{RT} \right) \tag{4.17}$$

- Concentration polarization

This polarization results from a partial pressure in porous electrode region reduce more than bulk gas outside this region and is brought to a gas transport loss. It can be estimated by Eqs. (4.18) and (4.19) for anode and cathode sides, respectively.

$$\eta_{conc,a} = \frac{RT}{2F} \ln \left[\frac{\left(1 + (RT/2F)(l_a / D_{a(eff)} p^I_{H_2O})i\right)}{(1 - (RT/2F)(l_a / D_{a(eff)} p^I_{H_2})i} \right] \tag{4.18}$$

$$\eta_{conc,c} = \frac{RT}{4F} \ln \left[\frac{p^I_{O_2}}{(p_c/\delta_{O_2}) - ((p_c/\delta_{O_2}) - p^I_{O_2}) \exp\left[(RT/4F)(\delta_{O_2} l_c / D_{c(eff)} p_c)i\right]} \right]$$

(4.19)

where δ_{O_2}, $D_{a(eff)}$ and $D_{c(eff)}$ are given by:

$$\delta_{O_2} = \frac{D_{O_2,k(eff)}}{D_{O_2,k(eff)} + D_{O_2-N_2(eff)}} \tag{4.20}$$

$$D_{a(eff)} = \left(\frac{p_{H_2O}}{P_a} \right) D_{H_2(eff)} + \left(\frac{p_{H_2}}{p_a} \right) D_{H_2O(eff)} \tag{4.21}$$

$$D_{c(eff)} = \frac{\xi}{n} \left(\frac{1}{D_{O_2,k}} + \frac{1}{D_{O_2-N_2}} \right) \tag{4.22}$$

$$\frac{1}{D_{H_2(eff)}} = \frac{\xi}{n} \left(\frac{1}{D_{H_2,k}} + \frac{1}{D_{H_2-H_2O}} \right) \tag{4.23}$$

$$\frac{1}{D_{H_2O(eff)}} = \frac{\xi}{n} \left(\frac{1}{D_{H_2O,k}} + \frac{1}{D_{H_2-H_2O}} \right) \tag{4.24}$$

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

$$D_{(eff)} = \frac{n}{\xi}D \tag{4.25}$$

Assuming straight and round pores, the Knudsen diffusion parameter can be calculated by:

$$D_{A,k} = 9700\sqrt{\frac{T}{M_A}} \tag{4.26}$$

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

$$D_{A-B} = 1.8583x10^{-3}\left(\frac{T^{3/2}((1/M_A)+(1/M_B))^{1/2}}{P\sigma_{AB}^2\Omega_D}\right) \tag{4.27}$$

where σ_{AB} is the characteristic length and Ω_D is the collision integral. These parameters are given by:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{4.28}$$

$$\Omega_D = \frac{A}{T_k^B} + \frac{C}{\exp(DT_k)} + \frac{E}{\exp(FT_k)} + \frac{G}{\exp(HT_k)} \tag{4.29}$$

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

$$T_k = \frac{kT}{\varepsilon_{AB}} \tag{4.30}$$

where k is the Boltzmann constant and ε_{AB} is the characteristic Lennard-Jones energy.

All the parameters used in this model are concluded in Table 4.1

Table 4.1 Summary of all parameters used in the SOFC model

Parameters	Value	Parameters	Value
L (μm)	50	σ_{H_2} (Å)	2.827
$E_{act,a}$ (J/mol)	1.0 x 10^5	σ_{H_2O} (Å)	2.641
$E_{act,c}$ (J/mol)	1.2 x 10^5	σ_{N_2} (Å)	3.798
γ_a (A/m^2)	1.344 x 10^{10}	σ_{O_2} (Å)	3.467
γ_c (A/m^2)	2.051 x 10^9	ε_{H_2}	59.7
l_a (μm)	750	ε_{H_2O}	809.1
l_c (μm)	50	ε_{N_2}	71.4
ξ (μm)	5.4	ε_{O_2}	106.7
n	0.48		

4.2.2 Calculation Procedure

The calculation begins with defining the desired values of fuel utilization of SOFC including operating voltage, temperature, and parameters of anode and cathode inlet flow rate in each gas component. Fuel utilization was divided into many small regions with step size of 0.01 in SOFC stack to calculate the current density and area in each region as illustrated in Figure 4.2.

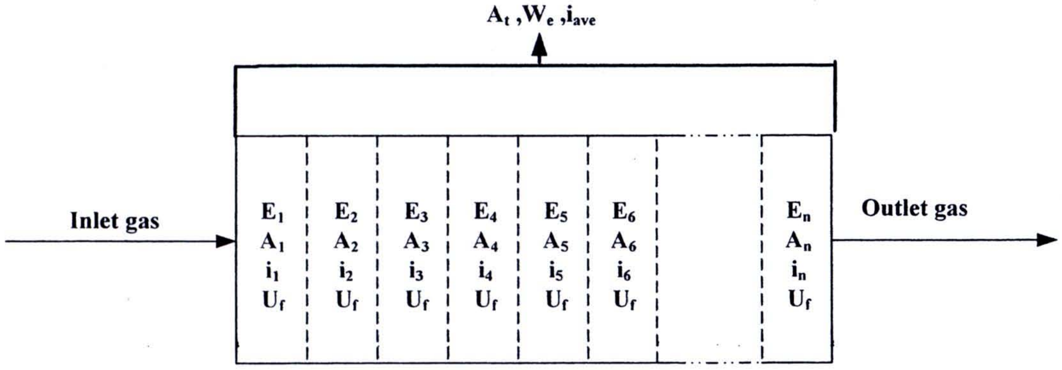

Figure 4.2 The schematic SOFC module for numerical calculation

The sets of equation in Section 4.2.1 are arranged and placed on the potential balance in Eq. (4.12). A constant operating voltage (V) is defined and open circuit voltage (E) is early computed. Thereafter, the current density in each region is obtained by calculating with trial and error until the difference between E and the total polarizations is equal to the operating voltage (V) on Eq. (4.12). The small element of SOFC area can be calculated by the following equation:

$$A_f = \frac{2F(\Delta U_f)}{i_f} \tag{4.31}$$

The numerical calculation is continued until the value of U_f reaches the desired fuel utilization. The total SOFC area (A_{total}) can be obtained by summation of each small area (A_f). Then, the average current density (i_{ave}), power density (p_{ave}) and total electrical power (W_e) are calculated with Eqs. (4.32), (4.33) and (4.34), respectively.

$$i_{ave} = \frac{2F(U_f)}{A_{total}} \tag{4.32}$$

$$p_{ave} = i_{ave} V \tag{4.33}$$

$$W_e = p_{ave} A_{total} \tag{4.34}$$

The computational algorithm for determining SOFC performance is expressed as Figure 4.3.

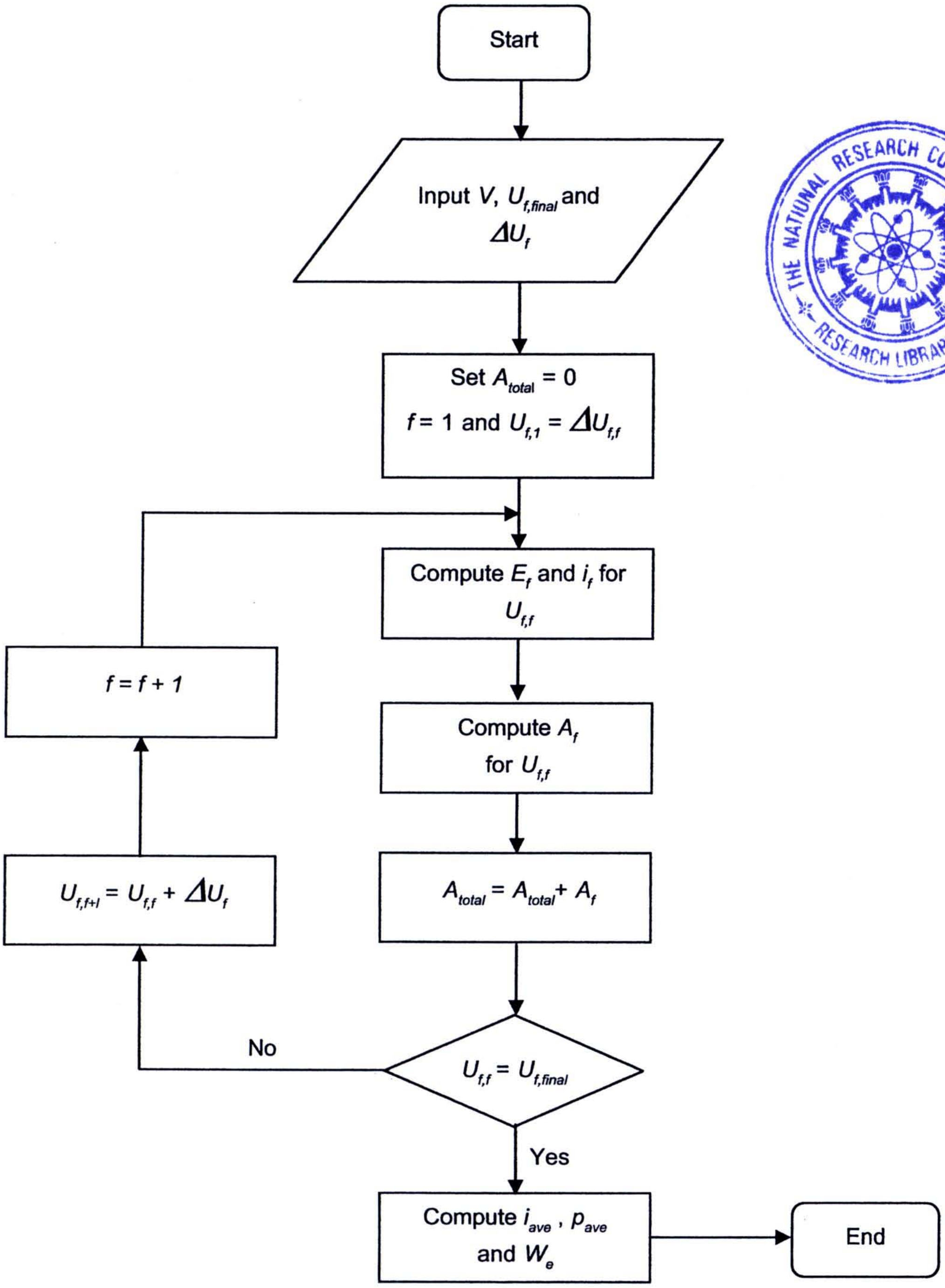

Figure 4.3 The flow chart of algorithm for computation of a fuel cell

4.3 SOFC system configurations

The process of SOFC system fuelled by bioethanol fundamentally consisted of preheaters, reformer, SOFC, and afterburner. In this research, the extra bioethanol pretreatment unit is further installed into this system as schematically shown in Figure

4.4. Bioethanol solution of 10wt% or 4.16mol% is introduced into a pretreatment unit operated under 348 K to carry out a desired ethanol concentration of 25 mol%, a stoichiometric ratio for ethanol steam reforming reaction in Eq. (2.7).

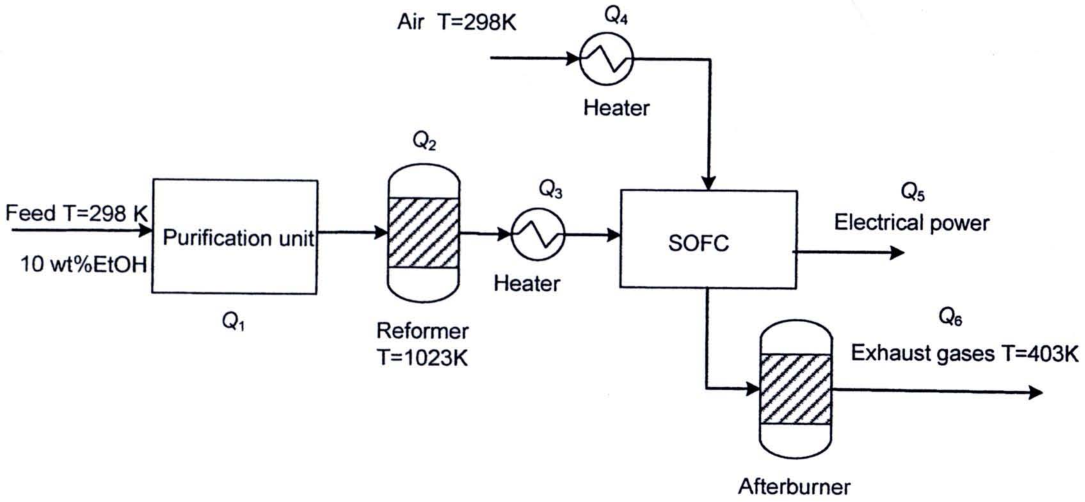

Figure 4.4 Schematic diagram of bioethanol-fuelled SOFC system

Afterwards, the stream with 25 mol% ethanol is fed into an external reformer operated at 1023 K under thermodynamic equilibrium condition. Ethanol steam reforming reaction is considered as a main reaction for producing hydrogen rich gas and the reactions in Eqs. (2.8) and (2.9) are defined as undesired reactions occurring simultaneously with the main reaction including water gas shift reaction as shown in Eq. (2.22). These reactions are assumed to take place isothermally in an external reformer simulated by Aspen plus. The reformed hydrogen rich gases are fed into an ER-SOFC to produce electrical power at the anode chamber whilst excess air (5 times) is preheated and fed into the cathode chamber. Exhausted gases released from an SOFC containing unreacted fuels are brought into the afterburner to combust and recover heat from this residue to supply energy to the other heat-demanding units i.e. purification unit, reformer, and preheaters. From Figure 4.4, the heat obtained from SOFC and the afterburner represented as Q_5 and Q_6 are assigned to have a role for supplying thermal energy to the heat-demanding units represented in Q_1, Q_2, Q_3 and Q_4. The final temperature of exhausted gases vented to the environment is specified at 403 K. In some cases, the overall performance of SOFC system is evaluated under the condition of no external energy demand or $Q_{net} = 0$ calculated by conventional energy balance as below:

$$Q_{net} = Q_5 + Q_6 - Q_1 - Q_2 - Q_3 - Q_4 = 0 \tag{4.35}$$

and the definition of overall electrical efficiency of this system is given by:

$$\eta_{elec,ov} = \frac{W_{e,net}}{mol_{EtOH} \cdot LHV_{EtOH} + External\ Heat\ Demand} \tag{4.36}$$

where $W_{e,net}$ is the net electrical energy gained from the system after subtracting power consumption of vacuum pump. LHV_{EtOH} is the lower heating value of bioethanol feed. According to Eq. (4.35), when $Q_{\mathrm{net}} < 0$, the SOFC system requires additional thermal energy from an external source and these amounts of heat are taken into account as external heat demand term in Eq. (4.36) of overall electrical efficiency.