

**Decarbonising the energy system with an integrated high temperature electrolyser and
fuel cell**

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ABSTRACT

This thesis presents an innovative integrated power-to-gas (PTG) energy system, primarily focusing on decarbonising the power generation sector and heating networks. It introduces a system-level simulation model combining Solid Oxide Electrolysers (SOEs), Molten Carbonate Fuel Cells (MCFC), Solid Oxide Fuel Cells (SOFC), and a methanation unit. The study explores the system's ability to produce electrical energy, methane, oxygen, biomethane, and thermal energy, thus contributing to sustainable and clean energy production aligned with the seventh UN Sustainable Development Goal, which emphasises 'Clean Energy'.

The research demonstrates over 85% CO₂ separation using an MCFC for upgrading raw biogas and methane production. A comprehensive techno-economic analysis of the fuel-cell-based PTG integrated energy system is conducted, focusing on thermodynamic efficiency and economic viability. The study also highlights the potential of leveraging in-situ CO₂ for PTG technology through the upgradation of raw biogas.

The proposed system achieves significant efficiencies: an energy efficiency of 79.7% and an exergy efficiency of 55.5%. It is economically viable, with a calculated levelised cost of energy (LCOE) of £72.2 per MWh and a payback period of 2.92 years. The system model is detailed and validated using data from literature, and it integrates various subsystems, each with its flowsheet and auxiliary units, into a novel PTG energy system.

The thesis concludes by identifying challenges in commercialising cost-effective fuel cell technologies and the uncertainties in energy demand. Future research directions include conducting in-depth analyses using real-world energy demand data, exploring the integration with a steam turbine for enhanced power generation, and conducting experimental tests to validate the model and assess the impact of pollutants on cell performance and lifespan. This research opens new avenues for various engineering fields by integrating sustainable practices into project designs and contributes significantly to the power-to-gas field.

DEDICATION

This thesis is dedicated to my late grandfather, Alhaji Sheikh Abubakar Babatunde Mohammed Al-Adabiy popularly known as Alhaji Ado, whose wisdom and guidance continue to inspire me. His legacy is a beacon that has illuminated my path throughout this journey.

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LIST OF SYMBOLS

$E_{a,i}$	Activation energy of i (i.e., anode or cathode) ($\text{J mol}^{-1} \text{ K}^{-1}$)
$E_{a,an}$	Activation Energy of the anode (Jmol^{-1})
$E_{act,an}$	Activation Energy of the anode (Jmol^{-1})
$E_{a,cat}$	Activation Energy of the cathode (Jmol^{-1})
$E_{act,cat}$	Activation Energy of the cathode (Jmol^{-1})
E_{act}	Activation energy overpotential
V_{MCFC}	Actual MCFC cell voltage
AECs	Alkaline Electrolysis Cell
An-in	Anode inlet
An-out	Anode outlet
T_{avg}	Arithmetic average of cathode inlet and exit temperature (k)
APMD	Aspen plus model data
P_{atm}	Atmospheric pressure.
r	Average pore radius of the electrodes (m)
BoP	Balance of plant
Biogas-1	Biogas type 1
Biogas-2	Biogas type 2
U_{OX1-CO_2}	Carbon dioxide utilisation factor
A	Cell area (m^2)
$I_{mcf c}$	Cell current
I	Cell current (A)
j_0	Cell exchange current density (Am^{-2})
R_{ohm}	Cell ohmic resistance
P	Cell operating pressure (bar)
T	Cell operating temperature (K)
V	Cell potential (V)
OX1-CO2	CO ₂ source
CHP	Combined heat and power
CNG	Compressed natural gas
Z_{Anode}	Concentration and activation polarisation occurring at the anode
$Z_{Cathode}$	Concentration and activation polarisation occurring at the cathode
E_{conc}	Concentration overpotential
Cl	Confidence level
I-V	Current - Voltage
J-V	Current density - Voltage
j	Current density (Am^{-2})
j	Current density (Am^{-2})
Φ_D	Dimensionless diffusion collision integral
DC	Direct Current
$D_{O_2}^{eff}$	Effective diffusion coefficient of oxygen (m^2s^{-1})
$D_{H_2O}^{eff}$	Effective diffusion coefficient of steam (m^2s^{-1})
D_x^{eff}	Effective diffusion of x (i.e., Colliding species O ₂ , N ₂ , H ₂ O and H ₂)
$\eta_{CO_2,captured}$	Efficiency of CO ₂ removal
EH	Electric heater
P_{elect}	Electrical power demand (W)

$P_{elect,mcfc}$	Electrical power released by the MCFC (W)
PTG	Power-to-gas
$\wp$	Electrode porosity
ξ	Electrode tortuosity
L	Electrolyte layer thickness (m)
$\Delta H_{water_splitting}^0$	Enthalpy change of water splitting reaction
$\Delta S_{water_splitting}^0$	Entropy change of water splitting reaction
E_{eq}	Equilibrium potential
$J_{0,i}$	Exchange current density (Am^{-2}) at i (i.e., cathode or anode)
$J_{0,an}$	Exchange current density of the anode (Am^{-2})
$J_{0,cat}$	Exchange current density of the cathode (Am^{-2})
T^s	Exit temperature (K) of the cathode
F	Faraday's constant, 96485 C mol^{-1}
F	Faraday's constant, 96485 C mol^{-1}
Flue gas-1	Flue gas type 1
Flue gas-2	Flue gas type 2
k_i	Frequency factor at i (i.e., anode or cathode (Am^{-2}))
j_l	Fuel cell's limiting current density
U_f	Fuel utilisation factor
$\Delta G_{water_splitting}^0$	Gibbs free energy of water splitting reaction
GHGs	Greenhouse gases
HE	Heat exchanger
Q_O	Heat of oxidation reaction
Q_S	Heat of steam reforming reaction
Q_W	Heat of water-gas shift reaction
H	High
HM-Cath-in	High temperature MCFC cathode inlet
H-RBio	High temperature raw biogas
a_i and a_j	Independent variables or factors
Q_I	Initial heat of the fresh fuel, oxygen, and carbon dioxide source streams
n_{OX1-CO_2}	Inlet molar flow rate of the CO_2 source
T_c^{in}	Inlet temperature (K) of the cathode
β_{ij}	Interaction coefficient for the pairs of factors a_i and a_j
β	Intercept term
R_{int}	Internal resistance
$D_{x,k}$	Knudsen diffusion of x
ε_v/k	Lennard-Jones potentials of v (K)
ε_x/k	Lennard-Jones potentials x (K)
β_i	Linear coefficient for the factor a_i
L	Low
LHV	Lower heating value
LHV_{fuel}	Lower heating value of the fuel
M-Anode	MCFC anode
M-CATHODE	MCFC Cathode
MCFC	Molten carbonate fuel cell
MCATH-IN	MCFC cathode inlet
M-Elect	MCFC electrolyte
MS	MCFC Stream

σ_v	Mean diameter (m) for specie v
σ_x	Mean diameter (m) for specie x
$CO_{2,in}$	Molar flow rate of CO_2 available in the CO_2 source
$CO_{2,consumed}$	Molar flow rate of CO_2 consumed in the electrochemical reaction
$nCO_{2,required}$	Molar flow rate of CO_2 required for the electrochemical reaction
$\dot{n}_{fuel}$	Molar flow rate of fuel (mols^{-1})
$nH_{2,in}$	Molar flow rate of hydrogen available in the fuel
$nH_{2,spent}$	Molar flow rate of hydrogen consumed in the electrochemical reaction
$nO_{2, required}$	Molar flow rate of oxygen required for the electrochemical reaction
$\dot{n}_{H_2}$	Molar flow rates of hydrogen consumed (mols^{-1})
$\dot{n}_{H_2O}$	Molar flow rates of steam feed (mols^{-1})
M_v	Molar mass of v (gmol^{-1})
M_x	Molar mass of x (gmol^{-1})
$n_{H_2,out}$	Mole flow rate of hydrogen
y_{CO_2}	Mole fraction of carbon dioxide
y_{O_2}	Mole fraction of oxygen
$x_{i,Cathode}^s$	Mole fraction of the specie i at the cathode exit
$x_{i,Cathode}^{in}$	Mole fraction of the specie i at the cathode inlet.
$x_{i,Anode}$	Mole fraction of the specie i at the anode
$x_{i,Cathode}$	Mole fraction of the specie i at the cathode
D_{v-x}	Molecular diffusion coefficients of v and x (m^2s^{-1})
MCFC	Molten carbonate fuel cell
MCFC	Molten Carbonate Fuel Cells
MP	Multi-objective optimisation
n_e	Number of moles of electrons consumed per mole of hydrogen produced
n_e	Number of moles of electrons released per mole of Hydrogen consumed
OX2-O2	O_2 source
Q_{Gen}	Ohmic heating
E_{ohm}	Ohmic overpotential
OMP	Optimisation model prediction
U_{OX2-O_2}	Oxygen utilisation factor
Ppm	Part per million
P_{i,An_loss}	Partial pressure of the specie i at the anode for energy loss
P_{i,Cat_loss}	Partial pressure of the specie i at the cathode for energy loss
P_i	Partial pressure of the specie i
$P_{H_2}, P_{O_2}, P_{H_2O}$	Partial pressures of hydrogen, oxygen, and steam (kPa) respectively
PSA	Pressure Swings Adsorption
PEMECs	Proton Exchange Membrane Electrolysis Cell
β_u	Quadratic coefficient for the factor a_i
y	Response variable
V_{NST}	Reversible Nernst cell voltage (V)
$nCO_{2,elect.trans}$	Simulates the molar flow rate of CO_2 required to move through the electrolyte of the MCFC
$nO_{2,elect.trans}$	Simulates the molar flow rate of oxygen required to move through the electrolyte of the MCFC

SOE	Solid oxide electrolyser
Eff_{SOEC}	Solid oxide electrolytic cell's overall energy efficiency
SOFC	Solid Oxide Fuel Cells
E^0	Standard electrode potential (V)
$\Delta S_{H_2}^0$	Standard entropy of $H_{2(g)}$,
$\Delta S_{H_2O}^0$	Standard entropy of H_2O
$\Delta S_{O_2}^0$	Standard entropy of $O_{2(g)}$
$\Delta H_{H_2}^0$	Standard heat of formation of $H_{2(g)}$
$\Delta H_{H_2O}^0$	Standard heat of formation of H_2O
$\Delta H_{O_2}^0$	Standard heat of formation of $O_{2(g)}$,
Stm	Steam
U_{steam}	Steam utilisation factor
FR	Steam-to-hydrogen feed ratio
$Q_{Thermal}$	Thermal energy
Q_{loss}	Thermal energy loss
$Q_{Th,mcfc}$	Thermal energy released by the MCFC
$Q_{T\Delta S}$	Thermal energy required for the water splitting reaction
$Q_{An_preheat}$	Thermal energy required on the anodic side of the reaction
$Q_{Cath_preheat}$	Thermal energy required on the cathodic side of the reaction
d_{an}	Thicknesses of the anode (m)
d_{cat}	Thicknesses of the cathode (m)
Q_T	Total energy demand
$E_{T\ loss}$	Total overpotential losses
TS	Total solid
R	Universal gas constant, $8.314\text{ J mol}^{-1}\text{K}^{-1}$
UBIO	Upgraded biogas
V_{loss}	Voltage loss

CHAPTER 1: INTRODUCTION

1.1 Background

At present, fossil fuels are extensively utilised not only for energy production but also as raw materials in several chemical synthesis processes. As the world's energy demand continues to grow, the reliance on fossil fuels has led to the emission of large amounts of greenhouse gases and pollutants (such as particulates, sulphur oxides, and nitrogen oxides) which contribute to global warming and pose public health risks (1). The US and Europe were the main contributors of emissions until the second half of the 20th century, but have since been surpassed by Asia, particularly China. In 2017, Asia accounted for 53% of global emissions, with China being the largest emitter at 25% of global emissions. North America, dominated by the US, was the second largest regional emitter at 18% of global emissions, followed closely by Europe with 17%. In terms of per capita emissions, the highest emitters were major oil producing countries in the Middle East, while the United States, Australia, and Canada had the highest per capita emissions among more populous countries. However, there were large differences in per capita emissions between countries with similar standards of living, with some European countries having lower emissions than their neighbours. Many countries in Africa and South America had very low per capita emissions, with emissions from international aviation and shipping also contributing significantly to global emissions (2). Meeting the challenge of reducing CO₂ emissions will require not only increasing the use of zero or negative emission energy sources, but also decarbonising the global conventional energy systems. The target is to reach thermoneutrality by 2050, which means that human activities must emit the same amount of greenhouse gases (GHGs) as can be absorbed through GHG reduction measure (3).

While carbon capture technologies for fossil fuel combustion are still being developed and are currently costly (4–6), achieving this goal will require significant effort and investment.

The global generation of power from renewable energy sources continued to rise, reaching over 8 EJ and accounting for 5.8% of the record-breaking increase in 2021, surpassing 2019 levels by 1.3%. This constituted 18% of net power generation in 2022, largely driven by wind and solar energy (7) as technologies such as PV cells and wind turbines become more widely available. However, the fluctuating power output of these technologies (8) remains a challenge to their global deployment. Thus, researchers and policymakers continue to explore ways to enhance the availability of renewable energy production (9,10).

The key issues are power fluctuation, flexibility of the system and providing power when needed. There is a need to systematically store the excess energy available in peak power production periods in compensative measures against the lower energy production periods in order to aid the scale-up of employability of energy from renewables (11). As such, energy storage is considered a key technology as it can help provide an assuagement for the inherent deficiencies when integrating renewable power into the electrical grid (12,13). Various energy storage technologies based on their working principles are shown in Table 1.1.

Table 1.1: Energy storage techniques

Energy Form	Principles	Reference
Electrical	Superconducting magnetic energy storage (SMES), super-capacitors.	(14)
Mechanical	Flywheels, pumped storage, and compressed air.	(15)
Thermal	Thermochemical, sensible heat and latent heat	(16,17)
Chemical	Electrochemical, power-to-liquid/gas (P2L, PTG, P2X)	(18–20)

Asides the working principles, the techniques also differ in further aspects, such as mode of discharge, time requirement for start-up, capacity, operating conditions, bulkiness of the equipment involved, and efficiencies, involving the application of various disciplines to overcome the technical issues (21).

Energy storage by SMES, flywheels and super capacitors offer some advantages over the other storage technologies which includes high round-trip efficiency, low charging and response time, long life cycle, and high-power density. However, the major drawback of SMES and super capacitor is the cost of installation in comparison with the storage capacity (22), while flywheels are affected by standby losses. Both flywheel and super capacitor suffer from low energy density (23).

Pumped hydro power energy storage has the capability of high energy storage duration (for over 6 months) but still contributes to the emission of greenhouse gasses due to the released of CO₂ from cement production during construction (23). The major disadvantages of compressed air energy storage (CAES) are the dependence on geological formation and high installation cost (24).

The use of batteries for energy storage enjoins low maintenance requirement and high round trip efficiency but lacks high energy capacity and density and has an issue of self-discharge. Therefore limiting their utilisation to short term storage (18).

Easy transportation of energy to where it is needed is another topic of interest and the necessities to store excess renewable energy cannot be overemphasised. High energy and power density, utilisable for extended period of time can be achieved by employing power-to-fuel technologies (21).

The purpose of this chapter is to provide an overview of the concept and technology to be discussed in this thesis, as well as the structure of the thesis. The focus is on biogas upgrading

by removing CO₂ at no energy cost, feeding the upgraded biogas to the national grid, and generating electricity suitable for various applications.

1.2 Power-to-Gas (PTG)

In regions, where there is abundant solar or wind energy sources, one way to store excess energy is to employ the concept of Power-to-Methane (P2M) (25), and integrate it with high temperature fuel cells such as MCFC and solid oxide fuel cells (SOFCs) in such a way as to efficiently exploit the stored renewable energy. A P2M plant basically consists of a water electrolyser, a CO₂ source, and a methanation module as shown in **Figure 1.1** (26).

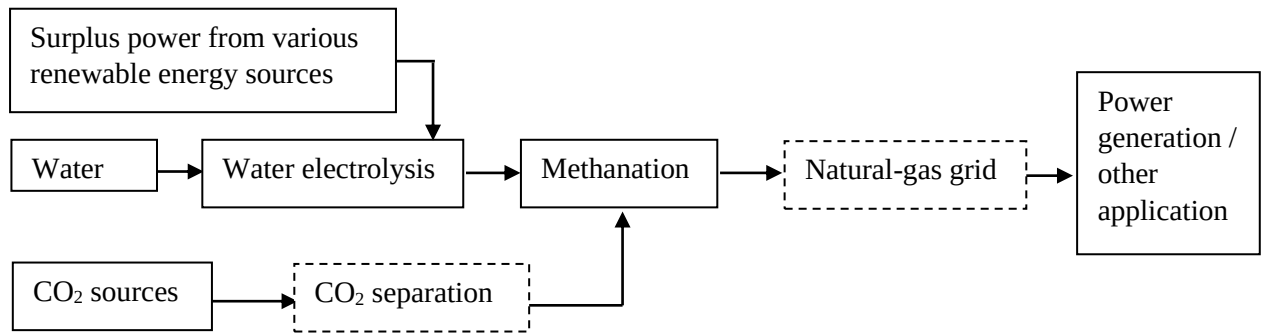


Figure 1.1: Principle of power-to-methane

Pure hydrogen gas is produced by the electrolyser from water and sent to the methanator. In the methanation unit, the pure hydrogen gas is reacted with CO₂ to generate a mixture of gasses which primarily consist of methane and steam (25). The reaction equations are presented in Equation (1.1) - (1.3). The methane gas obtained can be sent to storage or fed into the natural gas grid as pure methane to be later used, for example in SOFCs for power generation. Methane fuel is preferred because of its relatively higher hydrogen to carbon ratio compared to other hydrocarbon fuels (27).





CO₂ sources for the technology can include biomass plants (i.e. from biogas upgrading - approximately 100% (v/v) (28)), power generation plants (i.e. from combustion of coal – about 10-15% (v/v) (29), natural gas – about 3-5% (v/v), petroleum – about 3-8% (v/v), industrial processes (i.e. in the production of cement – about 14-33% (v/v) (30), production of ethylene oxide – approximately 100% (v/v), production of Iron and steel – about 20-30% (v/v) (30)) and ambient air – approximately 0.04% (v/v) (31).

The technical feasibility of CO₂ capture from these sectors is positive, however, the integration in the present technology is economically dependent on the CO₂ partial pressures in the exhaust gas due to the energetic and procedural effort for separation (30). Various CO₂ capturing technologies are discussed in the succeeding section.

1.3 Technologies for CO₂ capture

CO₂ is one the most important reactants after H₂, required probably in its highest purity form for the methanation process. It is desired to be obtained at low energy cost and at a reasonable flow rate (32). CO₂ is obtainable by carbon capture in fossil fuel powered plants and as an industrial process by-product through the chemical capture technologies shown in Table 1.2 with their respective energy requirement.

Inherent issues with the CO₂ capture or sources include high energy requirement as shown in Table 1.2, low efficiencies especially with physical or chemical absorption processes from ambient air, biogas plant limited capacities. Nevertheless, a key to achieving a high efficiency in the methanation reaction is the CO₂ percent purity (33). Common CO₂ sources, investigated in past studies are those from the combustion of coal, natural gas, or petroleum. Their integration with fuel cell plants particularly SOFCs is a breakthrough in achieving concurrently a huge fuel conversion efficiency and very low pollutants emission (34).

Table 1.2: CO₂ capture processes

Solvent group/Methods	Energy requirement (GJ/ton of CO ₂)	Reference
Amines / Amines + physical solvents/ Amines mixture	3.0 – 10.71	(35–39)
Aqueous Ammonia	3.69 - 4.07	(40)
Dual-alkali system (Chemical)	0.82	(41)
Adsorption	1 - 3	(42)
Cryogenic	0.395 – 3.4	(43)
Membrane	1.1–1.9	(44–47)
Phase change materials	2.0 – 2.5	(48–52)
Ionic liquids (ILs)	1.4 - 3.2	(53–55)

This however eliminate the problem of transporting CO₂ to the site. Nevertheless, the energy requirement for the CO₂ separation still makes it somewhat less energy efficient.

This PhD thesis aims to propose and evaluate a new process that can significantly address the energy requirement issue. The proposed process involves using MCFC as a carbon capture unit in an integrated system where energy integration is of central importance. To achieve this target, a flexible simulator based on traditional flowsheeting platforms was developed as a key contribution of this project.

1.4 The overall plant layout for the system proposed in this thesis

Figure 1.2 depicts the overall layout for the proposed power-to-gas energy system plant, presenting a system that uses biogas input and CO₂ recycling via an MCFC unit. Water and biogas are used as input to an SOE and an MCFC, respectively, as shown in the flow chart in **Figure 1.2**. The SOE₁ produces pure hydrogen gas, which is delivered to the MCFC anode. Biogas, which has already undergone a precleaning process, is supplied to the MCFC cathode through a mixer (MX-1) that proportionally mixes the biogas with pure oxygen released from the SOE₁ anode (air electrode). Here, the CO₂ is transferred to the anode by facilitating the oxygen ion diffusion necessary for the hydrogen oxidation reaction. The exit stream, containing steam and carbon dioxide, is then sent to condenser-2 to condense the steam and separate the

carbon dioxide, which is passed to the methanation reactor through mixer (MX-2) that proportionally mixes the carbon dioxide with the exit stream of the SOE₂ (primarily syn gas).

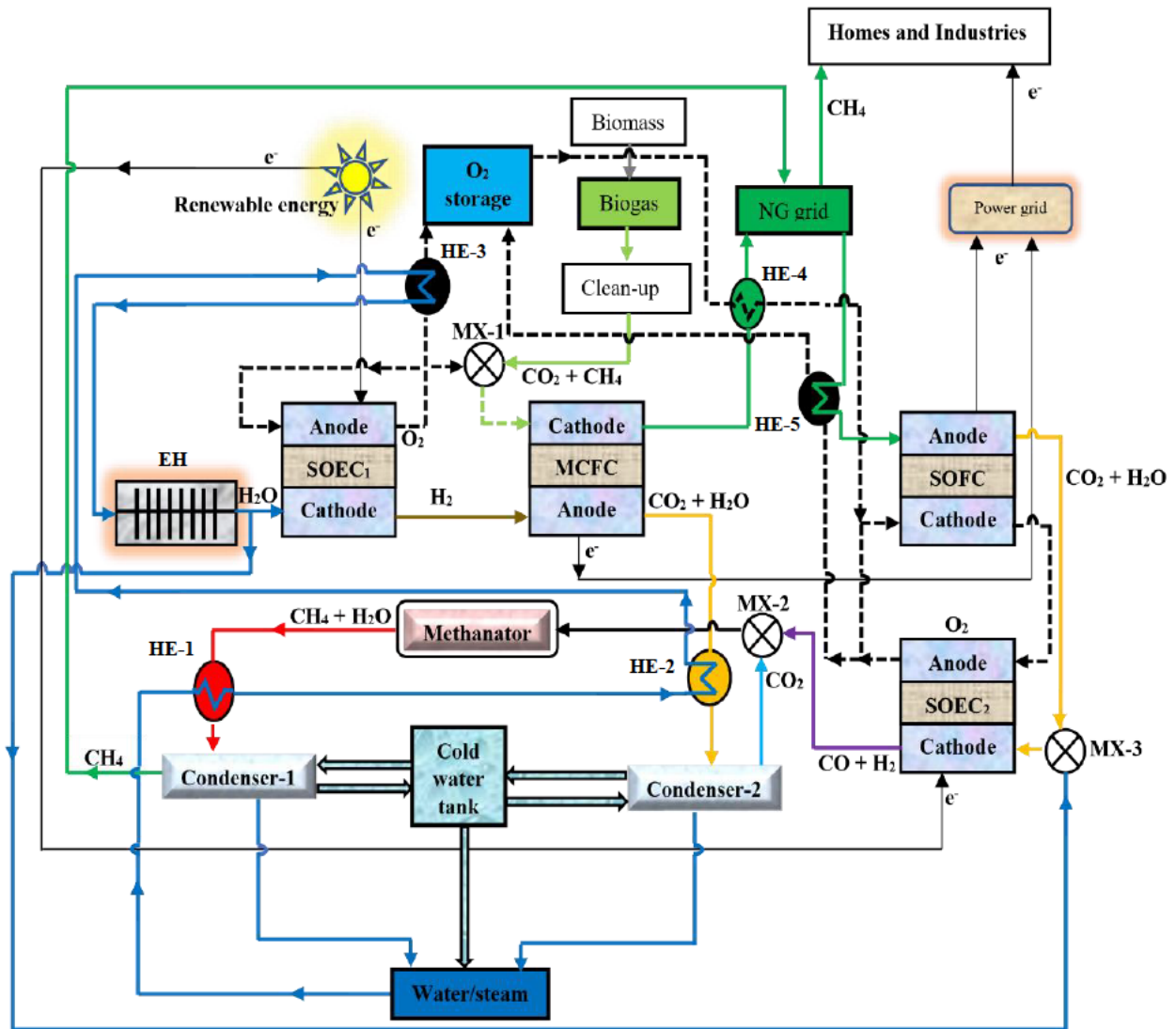


Figure 1.2: The layout for the proposed power-to-gas energy system plant.

In this way, close control is kept of the reactant gas flow compositions. The methane-enriched gas from the MCFC cathode effluent is first used to preheat the pure O₂ gas input from the O₂ storage tank sent to the SOFC cathode through the heat exchanger HE-4, which itself in turn cools down before being sent to the natural gas grid. Meanwhile, the methanation reactor outlet stream, which mainly comprises steam and methane gas, is passed through condenser-1 to separate the mixture and deliver pure methane gas, which is sent to storage or fed into the

natural gas grid. The steam utilised by the SOEs is generated by first preheating the water by passing it through several heat exchangers, namely HE-1, HE-2, and HE-3, before finally being sent to the heater (EH). The EH supplies steam to both SOE₁ and SOE₂.

On 'discharging' the gas storage by extracting methane from the gas grid and feeding this to the SOFC, the second SOE will be fed with the SOFC anode effluent composed mainly of CO₂ and H₂O. This, in turn, delivers syn gas (CO + H₂) for the methanation reactor. It is necessary to have control over the admissible H₂/CO ratio of 3:1 or H₂/CO₂ ratio of 4:1, which is an optimal ratio for production of methane and steam in the methanator. This is achievable by mixer MX-2, which proportionally mixes CO₂ and syngas before being sent to the methanator.

Explanations of reactions taking place in each unit and their significances in the configuration are discussed in the succeeding sections.

1.4.1 The SOE

The process begins with the electrolysis of water using the solid oxide electrolyzer-1 (SOE₁), as shown in **Figure 1.2**. This process is proposedly to use excess renewable energy from sources such as solar and wind to split water (H₂O) into hydrogen (H₂) and oxygen (O₂) (56). While co-electrolysis of a mixture of CO₂ and H₂O occurs in SOE₂ as shown in **Figure 1.2**. The principle of solid oxide electrolyzers (SOEs) is illustrated in **Figure 1.3**. H₂ (from SOE₁) and or CO (from SOE₂) are produced at the cathode while oxygen evolves at the anode. A solid electrolyte that is conductive only to oxygen ions (O²⁻) separates the two electrodes. The input gas stream for SOE₁ is composed of only steam, while SOE₂ includes both carbon dioxide and steam. The feed gas is proposedly to have access to electrons from excess solar and wind power, which produces either H₂ gas (in SOE₁, delivered to the MCFC anode in **Figure 1.2** or syngas (H₂ and CO) (in SOE₂, delivered to the methanation unit) as shown in Equation (1.4) and (1.5) (57).

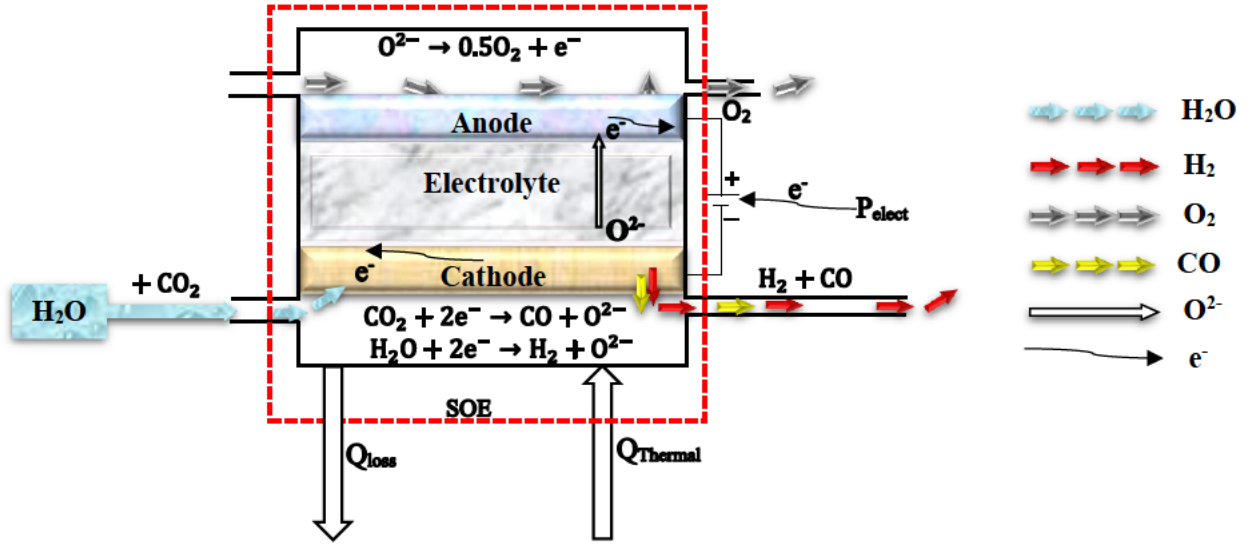
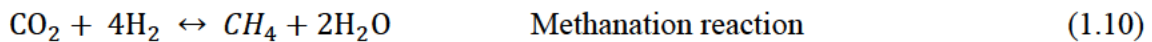
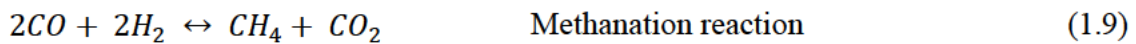
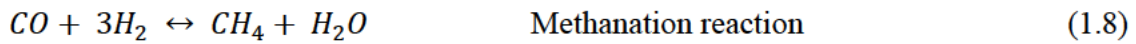
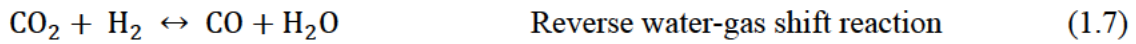


Figure 1.3: Schematic illustration of an SOE

The oxygen ions are transported through the solid electrolyte to the anode where they are oxidised to oxygen gas as shown in Equation (1.6) and sent to either the MCFC cathode (as in SOE₁) or storage tank (as in SOE₂) which can later be used in the SOFC.



The co-electrolysis of steam and carbon dioxide in SOE₂ is more complex compared to individual electrolysis of the feed in SOE₁. This is due to the potential reactions represented in Equation (1.7) - (1.10) that could take place on the cathode (58):



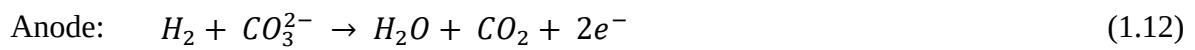
High-temperature steam electrolysis has the advantage of requiring less electrical energy compared to low-temperature electrolyzers (Alkaline and PEM), especially when the latent heat

of water vaporisation is provided from an external source. Several literature studies have found that electrolysis of steam at 1173.2K requires around 20% less electrical energy than electrolysis of water at 353.2K. This high-temperature steam requirement, however, facilitates thermal integration with the methanation reactor and thus reduces the need for additional cooling equipment. As a result, SOEs are a promising technology for this purpose, although the impact of high temperature and long-term operation on the durability of ceramic materials remains questionable (59).

1.4.2 Molten carbonate fuel cell

This study proposes the use of a Molten Carbonate Fuel Cell to supply CO₂ captured from biogas to the methanation reactor, providing a direct source of pure CO₂ for the reaction zone. The MCFC can also be used to improve biogas by removing CO₂.

In general, an MCFC uses CO₃²⁻ as an electron carrier through its molten carbonate electrolyte. When CO₂ gas is supplied to the MCFC cathode, it reacts with O₂ to form CO₃²⁻, which then diffuses to the MCFC anode where it is recovered as CO₂ after reacting with H₂, generating two moles of electrons, as shown in Equation (1.11) and (1.12).



In simpler terms, MCFCs can function as a gas filter and, when used to remove CO₂ from biogas in this study, can increase the heating value of the biogas while providing CO₂ at no energy cost for the methanation reaction.

1.4.3 Methanation unit

The syngas produced via the co-electrolysis of steam and CO₂ could as well be fed directly to the SOFC anode, instead of CH₄ but several studies (60–62) revealed low fuel conversion

efficiencies and high rate of air flow requirement for cooling the SOFC device when pure syngas is used as the fuel gas.

However, if a fraction or the whole fuel gas is made up of CH_4 , internal reforming of the CH_4 gas will be enhanced by the heat generated within the SOFC electrochemical reaction, this in turn causing cooling of the device. Therefore, more coolant like air would be required when fuel gas with zero percent methane is used which consequently reduces the efficiency of the fuel cell (60).

Methanation is an exothermic reaction (56) as shown in the following chemical equations Equation (1.1) to (1.3) with the reactor temperature ranging from 503 to 1023K and the process pressures ranging from 4.4 to 84 atm (63).

Thermodynamically, the reactions are favoured at low temperatures and high pressures.

The important criteria for designing an efficient methanator are listed as follows (64):

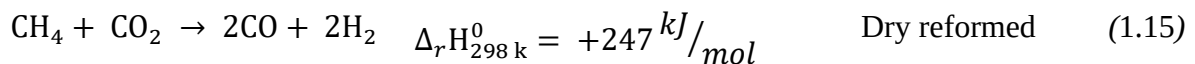
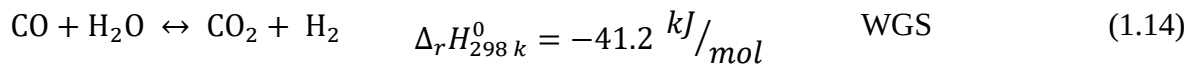
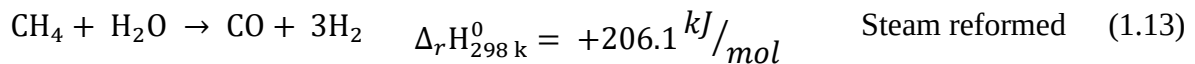
- (i) Operate at conditions that aid high methane yield and fast kinetics,
- (ii) Avoid catalyst deactivation caused by sulphur poisoning,
- (iii) Avoid conditions such as extremely low temperature or inadequate $\text{H}_2\text{:CO}$ ratio which can deactivate the catalyst by deposition of carbon and formation of Nickel tetra carbonyl ($\text{Ni}(\text{CO})_4$).
- (iv) Avoid sintering of catalysts at high temperature.

Considering the exothermic nature of the methanation reaction, the temperature conditions would appear difficult to achieve (64). Nevertheless, addition of Steam could help increase the H_2 and O_2 content of the feed syngas, thereby, lowering the risk of carbon deposition.

1.4.4 The SOFC

Solid oxide fuel cells (SOFCs) are high temperature (i.e. 500 to 900 °C) fuel-to-power devices (65) which accept directly not only hydrogen, but also hydrocarbons (66) such as CH₄, C₂H₅OH (67), C₃H₈ (68,69), or reformed CO(NH₂)₂ (70) as fuel for generation of power. Syngas (CO, H₂) and ammonia (NH₃) are also potential fuels.

The SOFC will be fed with the gas stream generated at the methanation unit which consist mainly of CH₄ and steam together with some percentage of unreacted CO, H₂ and even CO₂. SOFC can internally reform the methane gas as shown in Equations (1.13) to (1.15) (71) which practically overcomes the requirement for an external fuel reforming unit. External reforming will increase the cost and makes the operation complex, or could also reduce the plant's efficiencies (27).



The internal fuel reforming reactions represented in Equations (1.13) and (1.15) is enhanced by the heat generated by the electrochemical oxidation reactions of the fuel at the anode. However, in a typical SOFC operating condition, heat generated by the electrochemical reaction is higher than the heat required for the internal reforming reaction. This thereby still requires additional external cooling of the device but would have been lowered by 50% as compared to that required if external reforming reaction is used.

However, this mismatch in heat requirement and supply could give lead to non-uniformity in temperature distribution within the SOFC device which consequently could induced thermal stress on the cells and cause mechanical failure. Nevertheless, the above stated problem can be

attenuated through the addition of little amount of O_2 to the feed fuel (i.e. CH_4) (72). Product gas from the SOFC will be recycled by means of a blower and cooling the stream might not be necessary since high-temperature steam electrolysis is employed.

1.5 Preliminary Mole balance of the proposed plant

The mole balance of the proposed plant was carried out using Aspen PlusTM as shown in **Figure 1.4**. 1 mol/hr of water is fed into the SOE1 cathode and biogas containing 1 mol/hr of CH_4 and CO_2 each respectively is fed into the MCFC cathode. The stoichiometric chemical reactions elucidated in the preceding sections for each module were employed for the calculations. **Table 1.3** shows the mole balance of the MCFC CO_2 capture plant. According to the performed analysis, the total number of electrons spent and generated are 20 and 28 respectively. It is worth to note that the extra 8 electrons generated is as a result of the 1 mol/hr of CH_4 captured from the biogas by the MCFC. It is assumed that oxygen as oxidant for both MCFC and SOFC is abundantly available for the calculations.

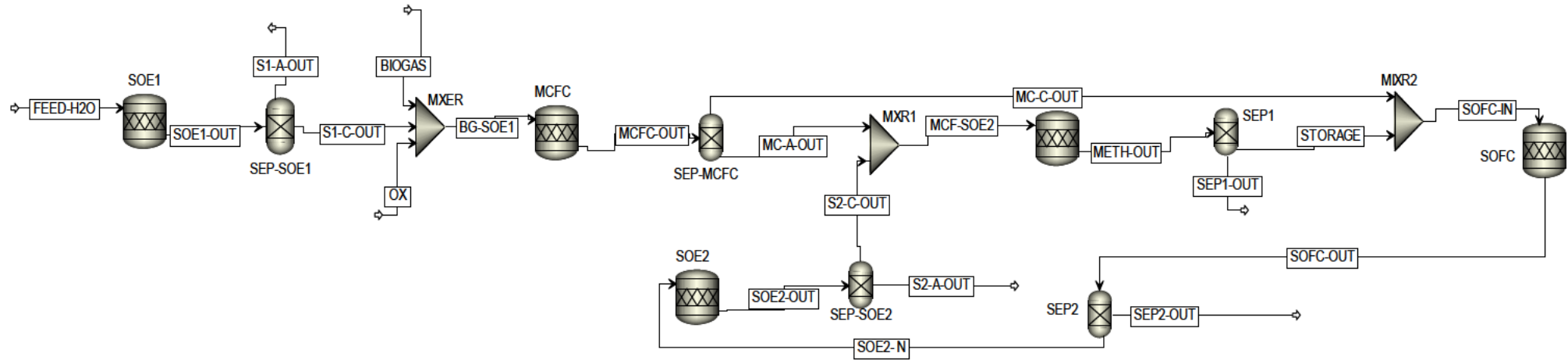


Figure 1.4: Aspen Plus flowsheet for the mole balance determination of the proposed power-to-Gas energy and decarbonisation system

Table 1.3: Mole balance of the proposed power-to-Gas energy and decarbonisation system

Mole flows											
Stream											
Name	Feed-H ₂ O	SOE1-out	Biogas	MCFC-Anode-out	MCFC-Cathode-out	MCFC-SOE2	Storage	SOFC-in	SOFC-out	SOE2-in	SOE2-Cathode - out
H ₂ O	1	0	0	1	0	1	0	0	6	6	0
H ₂		1	0	0	0	6	0	0	0	0	6
CO ₂		0	1	1	0	1	1	1	4	4	0
CH ₄		0	1	0	1	0	2	3	0	0	0
CO		0	0	0	0	4	2	2	2	0	4

1.6 Aims and Objectives

As shown in **Figure 1.2**, this thesis will focus on the following aims and objectives:

1.6.1 Aims

- Present an innovative integrated PTG energy hub system focusing on decarbonising the power generation sector and heating networks.
- Contribute to sustainable and clean energy production aligned with the seventh UN Sustainable Development Goal which emphasises 'Clean Energy'.
- Achieve a cost-effective CO₂ capture and generation of electricity.

1.6.2 Objectives

Chapter 1: Introduction

- Provide an overview of the power-to-gas concept and its significance in decarbonising energy systems.
- Outline the thesis structure and introduce the key components and technologies used in the proposed PTG system.

Chapter 2: Literature Review

- Review existing knowledge on CO₂ capture technologies and their integration with fuel cells.
- Identify gaps and trends in the field to establish the necessity and significance of the research.
- Highlight past studies and technological advancements related to PTG systems.

Chapter 3: Methodology

- Detail the techniques, approaches, and procedures used in the study, including the selection of tools for design, data collection, analysis, and interpretation.
- Introduce the modelling and simulation of fuel cells and related technologies using Aspen Plus.

Chapter 4: Modelling and Simulation of Solid Oxide Electrolyser for Hydrogen Generation

- Develop and validate a detailed model of a Solid Oxide Electrolyser (SOE) for hydrogen production.
- Conduct thermodynamic analysis and optimise the electrical and thermal energy requirements.
- Explore the effects of various operating parameters on SOE performance.

Chapter 5: Modelling and Simulation of Molten Carbonate Fuel Cell for CO₂ Capture

- Develop and validate a detailed model of a MCFC for CO₂ capture.

- Perform a sensitivity analysis to understand the impact of different fuel utilisation factors and oxidant sources.
- Compute the electrical and thermal energy outputs of the MCFC.

Chapter 6: Coupling of a Molten Carbonate Fuel Cell with a Solid Oxide Electrolysis Cell for Biogas and Flue Gas Decarbonisation: Feasibility Study and Process Effectiveness

- Propose and describe a novel process integrating MCFC and SOE for biogas upgrading and flue gas decarbonisation.
- Conduct simulations to evaluate the decarbonisation performance and system effectiveness.
- Assess the significance of the proposed process in the power-to-gas context.

Chapter 7: Modelling and Simulation of a Solid Oxide Fuel Cell

- Develop and validate a detailed model of a Solid Oxide Fuel Cell (SOFC) for power generation.
- Explore the effects of different operating parameters on SOFC performance.
- Conduct a sensitivity analysis to understand the impact of fuel utilisation factors, current density, and steam-to-carbon ratio.

Chapter 8: Modelling and Simulation of a Solid Oxide Electrolyser for Co-Electrolysis of Steam and CO₂ for Production of Syngas

- Develop and validate a detailed model of an SOE for co-electrolysis of steam and CO₂ to produce syngas.
- Conduct thermodynamic analysis and optimise the electrical and thermal energy requirements.
- Explore the effects of various operating parameters on the co-electrolysis process.

Chapter 9: Thermodynamic and Economic Assessment of a Fuel-Cell-Based Integrated Power-to-Gas Energy System

- Integrate all the individual modules (SOEs, MCFC, SOFC, and methanation unit) into a comprehensive PTG system.
- Conduct a thermodynamic analysis to evaluate the energy and exergy efficiencies of the proposed system.
- Perform a techno-economic analysis to assess the economic viability, including the levelised cost of energy (LCOE) and payback period.

Chapter 10: Conclusion and Outlook

- Summarise the outcomes of the thesis and discuss the findings.
- Highlight the significance of the research and its contributions to the PTG field.
- Provide recommendations for future work, including real-world energy demand analysis, integration with steam turbines, and experimental validation of the model.

1.7 Contribution to Knowledge

This thesis presents several novel contributions to the field of sustainable energy systems, particularly in the context of PTG technology and carbon capture. The key contributions are summarised as follows:

1. Development of an Integrated Power-to-Gas System:

- The research introduces an innovative PTG energy hub system that integrates SOEs, MCFCs, SOFCs, and a methanation unit. This system efficiently converts surplus renewable electricity into valuable energy carriers like hydrogen, methane, and thermal energy, significantly contributing to the sustainable and clean energy production goals aligned with the seventh UN Sustainable Development Goal (SuSDG).

2. High CO₂ Separation Efficiency:

- The study achieves over 85% CO₂ separation using an MCFC for upgrading raw biogas and producing methane. This high separation efficiency is critical for reducing greenhouse gas emissions and demonstrates the potential for MCFC technology in large-scale carbon capture applications.

3. Techno-Economic Analysis:

- A comprehensive techno-economic analysis of the proposed PTG system is conducted, focusing on its thermodynamic efficiency and economic viability. The system achieves an energy efficiency of 79.7% and an exergy efficiency of 55.5%, with a levelised cost of energy (LCOE) of £72.2 per MWh and a payback period of 2.92 years. These findings highlight the economic attractiveness and feasibility of the integrated energy system.

4. Optimisation of Electrolysis Processes:

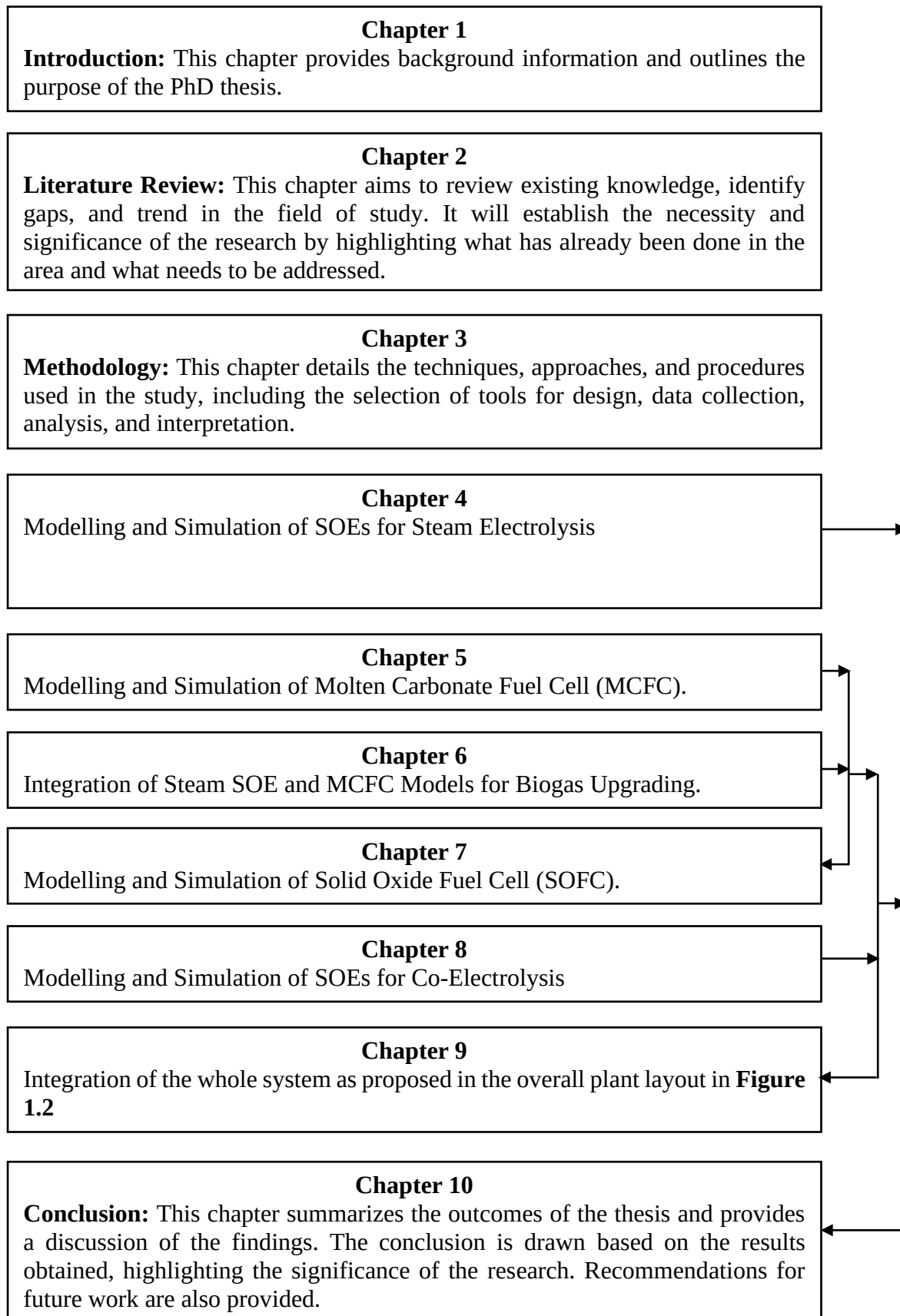
- The research develops detailed models for SOEs performing steam electrolysis and co-electrolysis of steam and CO₂. Through thermodynamic analysis and optimisation, the study enhances the understanding of the operational parameters affecting SOE performance, leading to improved energy and cost efficiencies.

5. Novel Integration Approach:

- A novel process integrating MCFC and SOE for biogas upgrading and flue gas decarbonisation is proposed. This integrated approach not only meets the quality standards for grid injection but also addresses the economic and technical challenges of integrating biogas into the grid, offering a sustainable solution for energy and environmental issues.

By addressing these key areas, this research makes significant contributions to advancing the understanding and implementation of integrated PTG systems, thereby supporting the transition to a sustainable energy future.

1.8 Thesis structure



CHAPTER 2: LITERATURE REVIEW

2.1 Background and Past studies

The International Energy Agency (IEA) reported in 2016 that 42% of global emissions were attributed to energy production (73). At present, the leading CO₂ capture methods for large power plants include post-combustion, pre-combustion, and oxyfuel combustion. Among these, post-combustion capture has seen the most extensive real-world application. However, these methods come with challenges, notably the significant energy consumption and the subsequent increase in the Levelised Cost of Electricity (LCOE). Therefore, innovative energy solutions like hybrid power cycles using fuel cells (FC) that offer both high efficiency and reduced CO₂ emissions are gaining attention and are subjects of extensive research and economic evaluations (74).

Many institutions and research institutes are geared towards the development of technologies such as the Integrated Gasification Fuel Cell Cycle (IGFC) that utilises low-cost fuels to generate electricity with high efficiency and eliminates the emission of greenhouse gases (GHGs) or incorporates carbon capture technology. The electrochemical oxidation of fuel in the FC provides an advantage over combustion engines as it only leaves CO₂ and H₂O as the exhaust, unlike combustion engines which produce oxides of sulphur and nitrogen. Several thermodynamic studies on the integration of gas turbines and FCs, particularly Solid Oxide Fuel Cell (SOFCs) and Molten Carbonate Fuel Cells (MCFCs), to form hybrid Fuel cell–gas turbine (FC-GT) cycles have been reported in literature over the last few decades. A concise overview of these studies is presented below.

Ghosh and De (75) conducted a study on the thermodynamic performance of a 20 MW_e IGFC system. The configuration included a gasifier through which oxygen was constantly supplied, an air separating unit, and a slurry feed. A syngas purifier with an operating temperature of

673.2 K was used to remove sulphur-containing compounds and particulates before being sent to the FC. The authors reported 48-55% lower heating value efficiencies, which varied with the cycle pressure (5 to 35 and cell potentials (0.91 to 0.965V).

Kivisaari et al. (76) performed a feasibility study on a high-temperature (HT) SOFC plant integrated with a coal gasifier. The study assessed a 30 MW_e system operating on a dry coal feed and oxygen-blown gasifier to produce syngas. The SOFC exhaust was used to reheat the syngas after quenching. The study showed 43% LHV efficiency without SOFC anode gas recirculation and 47% LHV efficiency with recirculation while assuming a cell voltage of 0.725V at fuel utilisation of 85%.

Verma et al. (77) reported a sensitivity analysis of a Vision 21 350 MWe coal power plant with CO₂ capture. The plant's configuration included a fluidised bed gasifier, a methanator, an Air separation unit (ASU), WGS reactors, a membrane-based H₂ separator, a catalytic combustor, a heat recovery unit, a CO₂ compressor and a SOFC fed with methane and recirculated H₂. The authors reported 51 to 53% LHV efficiency, while assuming 85% fuel utilisation, 0.75V cell potential and an operating pressure ranging from 5.9 to 19.7 atm.

In their study, Romano et al. (60) investigated a 590 MWe SOFC plant integrated with a coal gasifier, both with and without a syngas expander. The SOFC was supplied with syngas from the gasifier and pressurised air from the gas turbine compressor. Results showed a LHV efficiency of approximately 59% while achieving 85% fuel utilisation, a cell voltage of 0.753V, and a pressure ratio ranging from 20 to 26.5. The findings of the literature review, adding methanation or carbon capture units could enhance the plant configuration and increase efficiencies beyond the 60% threshold.

Grol et al. (78) conducted a study on a pressurised SOFC combined with a low-temperature (LT) catalytic gasifier, which produced a syngas containing approximately 18% methane. They

examined scenarios both with and without post-SOFC oxy-combustion for CO₂ capture. While they achieved LHV efficiencies of 59.2% without CO₂ capture and 62.4% with CO₂ capture, the study did not provide details on the LCOE.

Gerdes et al. (79) analysed the performance and LCOE of two SOFC-based IGFC power plants. One operated at atmospheric pressure (1.8 bar) and the other at pressurised conditions (18.9 bar). Both used an advanced catalytic gasifier and ensured low Sulphur levels in the FC feed gas. The atmospheric IGFC achieved a net efficiency of 49.4% HHV with an LCOE of \$88/MWh, while the pressurised IGFC had 56.2% HHV efficiency and an LCOE of \$79/MWh. Without carbon capture and sequestration (CCS), efficiencies would increase significantly.

Spallina et al. (34) thermodynamically analysed an SOFC-based plant with carbon capture. An air separator was used to produce pure oxygen for the gasification of coal. The syngas produced was cleaned and passed through heat recovery before being sent directly to the SOFC modules. The remaining combustible gas from the SOFC's anode exhaust was combusted with the pure O₂ from the ASU, and the product gas was used to generate steam by heat recovery before condensing and compressing the water and carbon dioxide respectively. The author fed coal with the captured CO₂ in the lock hoppers, avoiding the use of N₂ to achieve high CO₂ purity. The study of the 520 MW_e plant showed 47% LHV efficiency and approximately 0.0211 kg/kWh CO₂ emissions while maintaining 89% fuel utilisation and 0.747V cell potential in the SOFC. The study reduced CO₂ emissions, but the amount released will increase over time, and the plant did not provide for its reabsorption.

Romano et al. (61) also performed a thermodynamic study of an SOFC-based IGFC (coal-fuelled) plant integrated with H₂ post-firing, physical absorption carbon capture, and a methanator. The assessed plant gave 53% LHV efficiency and a specific CO₂ emission of 30.9% for a 582 MW_e system, maintaining 74% fuel utilisation and a cell potential of 0.812V

in the SOFC module. While the configuration achieved better CO₂ management with respect to net power, the high complexity of the plant incurred high equipment costs.

Siefert and Litster (80) explored pre-anode CO₂ capture in an IGFC using a Chemical Looping Combustion (CLC) method with a pressurised SOFC (5 bar). The process involved capturing CO₂ using magnesium and calcium oxide (MgO, CaO) at around 750°C. CO₂ regeneration occurred at 1000°C and 0.1 MPa, then compressed for storage. The efficiency achieved was 58% with a LCOE of \$52/MWh, considering EOR sequestration revenues, and \$60/MWh for saline sequestration.

Duan et al. (81) explored SOFC hybrid systems with CO₂ capture through oxyfuel combustion, emphasising turbine inlet temperature regulation. They examined steam injection, CO₂ gas injection, and heat exchange layout. For an SOFC unit around 142 MW, efficiencies were roughly 63% LHV, net. The study identified the SOFC stack, afterburner, and HRSG as primary sources of exergy loss. To boost system efficiency, they recommended research targeting these units, focusing on optimising temperature, pressure, and the utilisation factor (U_f) factor, which are crucial for overall performance.

Curletti et al. (82) assessed the technical and economic aspects of large biogas SOFC power plants with CO₂ capture, operating at both atmospheric and pressurised levels. Drawing insights from the SOFCOM project and Duan et al. (2013) (81), they explored various SOFC plant configurations and conducted a sensitivity analysis on U_f , stack temperature, and stack pressure. The studied SOFC module consistently generated 1MWe electrical power. The atmospheric reference scenario achieved a net efficiency of 48.4% HHV at a net present value (NPV) of \$0.6m. Pressurised scenarios, at low (2 atm) and high (6 atm) pressures, yielded efficiencies of 49.3% HHV and 48.9% HHV with NPVs of \$1.63m and \$1.86m, respectively.

Notably, pressurised setups outperformed atmospheric ones due to the supplementary electrical power generated by gas turbines or expanders.

Aghaie et al. (83) introduced an innovative system merging biomass gasification with a pressurised SOFC system (12 bar) using CLC and a steam power cycle. The process involves syngas from a gasifier (1400°C) pre-heating air for the SOFC cathode, while syngas from a reformer (950°C, 22 bar) feeds the anode. The anode's output gases undergo combustion in chemical looping reactors, and cathode's output powers a gas turbine. The system achieves a net efficiency of 55.8% and captures 100% of CO₂.

Campanari et al. (84) explored two plant designs: one combining an atmospheric pressure SOFC with a rankine cycle (SOFC+SC) and the other pairing a moderately pressurised stack with a brayton cycle (SOFC+GT). The atmospheric SOFC+SC achieved a net efficiency of 71.6% LHV, while the pressurised SOFC+GT reached 70.8% LHV. The latter's performance could be enhanced with an ORC bottoming cycle. However, CO₂ capture rates were capped at 82.4% for SOFC+SC and 81.4% for SOFC+GT due to cryogenic separation constraints. While these rates are below conventional CO₂ capture methods, they're notable for plant efficiency. A 90% CO₂ capture rate is attainable by increasing the U_f to 92%, though it might reduce efficiency.

Samanta and Ghosh (85) proposed a unique system to upgrade a thermal power plant by integrating both SOFC and MCFC before and after the existing boiler. In this setup, natural gas powers a direct internal reforming (DIR) SOFC module before the boiler. The SOFC's waste is then channelled to the boiler, replacing some coal energy. This SOFC system includes components like a stack, afterburner, and preheaters. The boiler's exhaust is directed to an MCFC, which has its own set of components, including a stack and heat exchangers. The

MCFC's anode off-gas undergoes combustion in pure oxygen, and the resulting CO₂ is compressed to 110 bars for storage and transport.

2.2 Sources of CO₂ Emissions

A substantial fraction of CO₂ emissions originates from large point sources such as power plants, petroleum refineries, and vast industrial facilities. **Table 2.1** shows the various sources of CO₂ emitted recognised. **Figure 2.1** Shows the proportion of anthropogenic CO₂ emissions attributed to electric power generation. The existence and locations of these facilities are influenced by various factors, including the distribution of natural resources and the economy of scale of operating large facilities. These large facilities often serve regions beyond their immediate locality, making the accounting of emissions complex (86).

Electric power generation is responsible for a significant portion of global CO₂ emissions. In the U.S., over 53% of fossil-fuel-derived CO₂ emissions are attributable to electricity generation and other large industrial facilities. About 35% of global fossil energy consumption comes from electric power generation, accounting for 26% of total global CO₂ emissions. Coal dominates the power sector, followed by natural gas and oil. Traditional thermal power plants using single cycle steam turbine technology are prevalent. However, combined cycle gas turbine power plants, which utilise both gas and steam turbines, are becoming more popular due to their higher efficiency (87,88). Various industrial processes produce CO₂ as a by-product. Globally, cement production is the largest industrial process emission source, releasing nearly 900 kg of CO₂ for every 1000 kg of cement produced. Refineries, especially those along the Gulf of Mexico, are significant contributors. Gas-fired process heaters and steam boilers are the primary emitters in refineries. The primary steel-making process, where melted iron ore reacts with CO gas, produces pure iron and CO₂. Petrochemical processes,

especially the production of ethylene and ammonia, are also notable sources of CO₂ emissions (88).

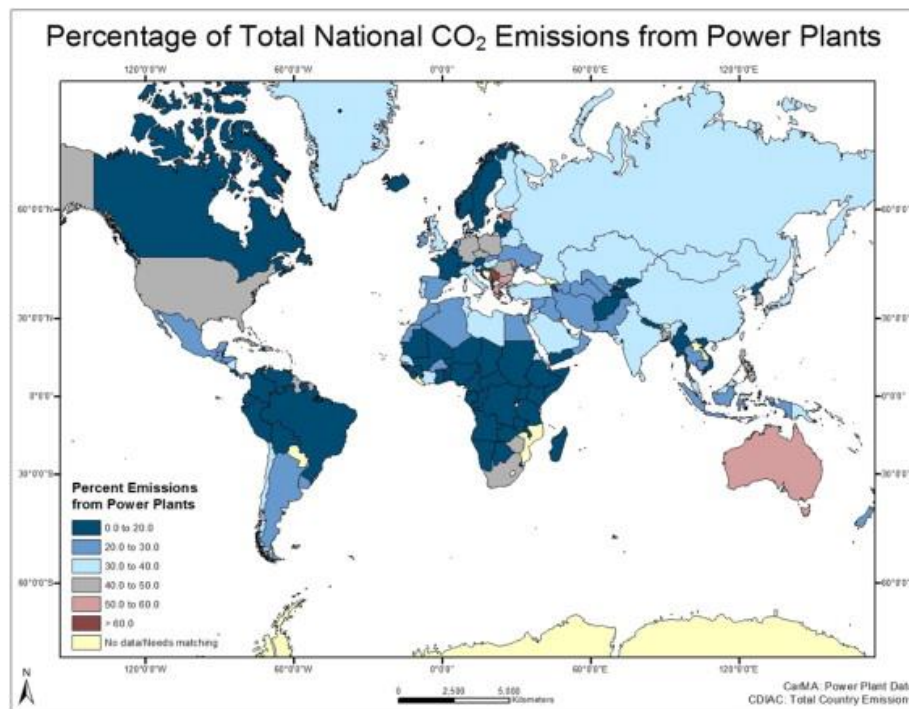


Figure 2.1: Proportion of Anthropogenic CO₂ Emissions Attributed to Electric Power Generation, 2009 from (89)

The combustion of fossil energy carriers in the transport sector accounts for about 14% of global greenhouse gas emissions. Direct capture and storage of these emissions are not practically feasible. However, a shift from fossil fuels to electricity or hydrogen in transportation can indirectly reduce emissions if the power comes from renewable or nuclear sources. If the electricity is derived from fossil fuels, capturing CO₂ from power plants can serve as an indirect measure to cut emissions from the transport sector (88).

Natural sources of CO₂, such as respiration by plants and animals, volcanic eruptions, and the release of CO₂ from oceans, have always been a part of the Earth's carbon cycle. While these sources contribute to the overall CO₂ levels in the atmosphere, the rapid increase in atmospheric CO₂ concentrations in recent decades is primarily attributed to human activities rather than natural processes.

Table 2.1: Summary of the Sources of CO₂ emissions and their respective application

CO₂ Emission Sources	Application/Description
Large Point Sources	Include power plants, petroleum refineries, and vast industrial facilities.
Electric Power Generation	Responsible for over 53% of fossil-fuel-derived CO ₂ emissions in the U.S. Dominated by coal, followed by gas and oil.
Cement Production	Largest industrial process emission source, releasing nearly 900 kg of CO ₂ for every 1000 kg of cement produced.
Petroleum Refineries	Significant contributors, especially those along the Gulf of Mexico. Gas-fired process heaters and steam boilers are primary emitters.
Steel-making Process	Produces pure iron and CO ₂ when melted iron ore reacts with CO gas.
Petrochemical Processes	Production of ethylene and ammonia are notable sources of CO ₂ emissions.
Transportation	Combustion of fossil energy carriers in transport accounts for about 14% of global greenhouse gas emissions.
Natural Sources	Include respiration by plants and animals, volcanic eruptions, and release of CO ₂ from oceans.
Biogas Upgradation Process	Removal of CO ₂ from biogas to increase the methane content, making it suitable for use as a vehicle fuel or for injection into the natural gas grid.

2.3 Technological Review for CO₂ Capture Technologies

This section explores the diverse techniques currently employed for capturing CO₂. It elucidates the intricacies of each technology and evaluates their associated costs. Furthermore, the section sheds light on recent advancements, strategies for CO₂ sequestration, and the prevailing policy framework governing their implementation.

Addressing the escalating concerns of climate change, capturing CO₂ has emerged as a pivotal strategy and the foundational stage in mitigating greenhouse gas emissions. A myriad of techniques has been developed to achieve this, each with its unique advantages and challenges. Broadly categorising, there are four predominant technologies that have garnered significant

attention: Post-combustion, Pre-combustion, Oxy-fuel combustion, and Direct air capture (DAC). Each of these technologies offers a distinct approach to the common goal of reducing atmospheric CO₂ concentrations.

2.3.1 Post-combustion Capture Scheme

This involves capturing CO₂ after combustion processes, typically using solvents. The process is generally uneconomic as it requires large equipment size and intensive energy input. The monoethanol amine (MEA) process, which is the most extensively studied CO₂ absorption system, allows the MEA solution to be contacted with flue gas in an absorber where CO₂ is absorbed by the solution. The CO₂-rich MEA solution is then sent to a stripper where it is reheated to release almost pure CO₂ (86) as shown in **Figure 2.2**. This scheme is retrofittable to the present large point sources of CO₂ which include power plants, refineries, natural gas sweetening, cement industries, petrochemical industries, iron and steel industries, and other heavy industries where fossil fuels are the main energy sources (90–92).

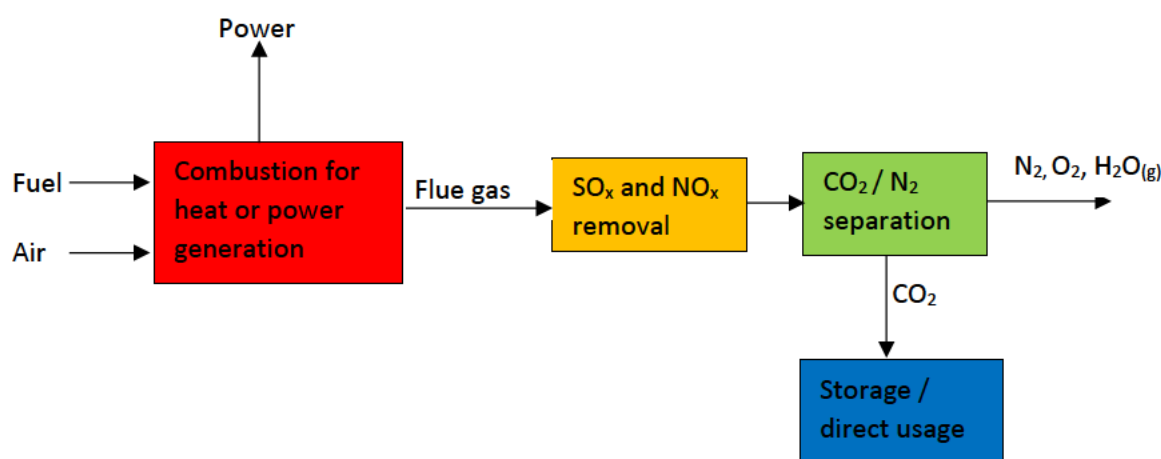


Figure 2.2: Post-combustion CO₂ capture scheme

2.3.2 Pre-combustion Capture

This process involves removing CO₂ before the combustion process, often in gasification processes. It is a proactive approach to reduce emissions by capturing CO₂ before it is released

into the atmosphere (93). It involves the partial oxidation or gasification of fuel, producing mainly CO and H₂ with minimal CO₂. The resultant mixture undergoes a water gas shift reaction, converting CO to CO₂ (20-40%) and increasing hydrogen production (55-80%) (94). The flue gas also contains nitrogen, steam, carbon monoxide, and hydrogen sulphide (95–97). CO₂ and H₂ are then separated; CO₂ is stored or utilised, while hydrogen is used for electricity generation, either by combustion or in FCs as shown in **Figure 2.3** (98). This method requires less energy for solvent regeneration than post-combustion capture but has higher capital costs (91,99).

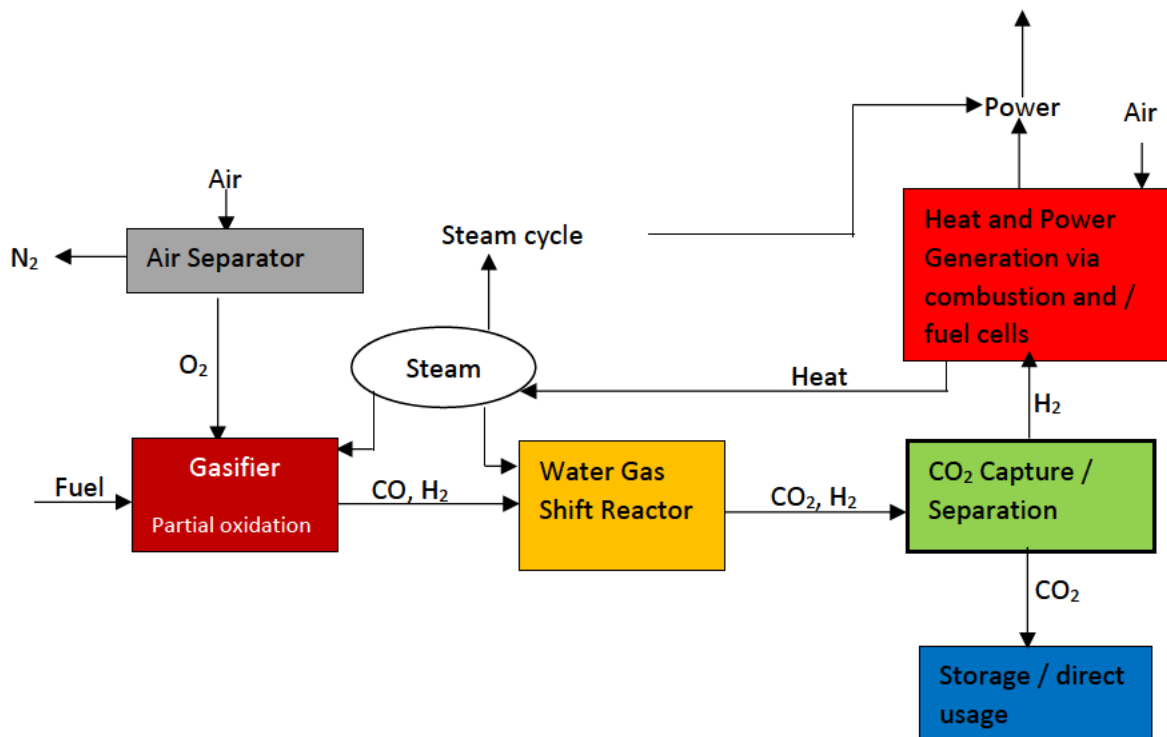


Figure 2.3: Pre-combustion CO₂ capture scheme

2.3.3 Oxy-fuel Combustion

This method involves burning fuel in pure oxygen to produce a CO₂-rich flue gas, which can then be captured. The combustion process in the presence of pure oxygen results in a flue gas that is primarily CO₂, making it easier to capture and sequester as shown in **Figure 2.4**

(100,101). Frequently, efforts are made to recover waste heat by recycling it in a combustor. The primary drawback of the oxy-fuel combustion CO₂ capture scheme is that the production of O₂ is both energy and capital intensive.

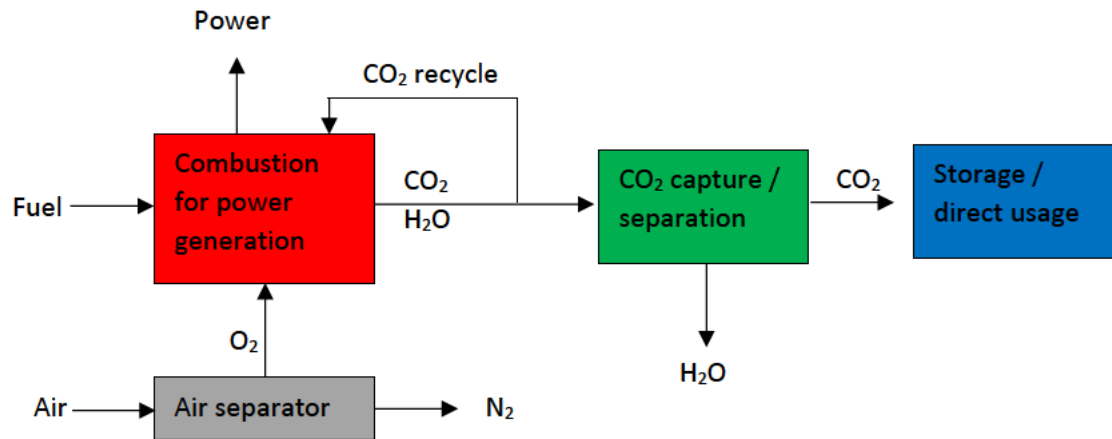


Figure 2.4: Oxy-combustion CO₂ capture scheme

2.3.4 Comparative Analysis of CO₂ Capture Technologies scheme

The various CO₂ capture technology schemes discussed, each with their unique set of advantages and challenges. The table below provides a comparative analysis of the four prominent CO₂ capture technologies schemes, highlighting their respective benefits and limitations.

Table 2.2: Comparative analysis of CO₂ capture technologies scheme

Technology	Advantages	Disadvantages
Post-combustion Capture	- Can be retrofitted to existing power plants. - Mature technology with commercial applications.	- Requires energy for solvent regeneration. - Solvent degradation can occur.
Pre-combustion Capture	- Produces hydrogen which can be used for electricity generation. - Lower energy requirement for solvent regeneration due to higher CO₂ partial pressures.	- High capital cost for facility construction. - Complex process with multiple steps.

Oxy-fuel Combustion	- Produces a high concentration of CO₂ in the flue gas, simplifying capture. - Potential for heat recovery.	- Production of O₂ is energy and capital intensive. - Potential for increased NO_x emissions.
DAC	- Can be deployed in various locations. - Not dependent on emission sources. - Potential for lower costs with LT options and waste heat utilisation.	- High energy requirement. - Still in developmental stages with limited commercial applications.

2.4 CO₂ separation technologies

As the world grapples with climate change challenges, separating CO₂ from gas streams has become a crucial solution. Various physical and chemical methods have been devised to tackle this issue, including Absorption, Adsorption, Chemical looping conversion, Cryogenic processes, Membrane technologies, and biological systems. Each method presents its own set of advantages and challenges in the pursuit of reducing CO₂ emissions. The selection of an appropriate technology hinges on the characteristics of the flue gas stream and, consequently, on the power plant's technology. **Figure 2.5** provides a comprehensive overview of the technologies, which will be further discussed in the subsequent sections.

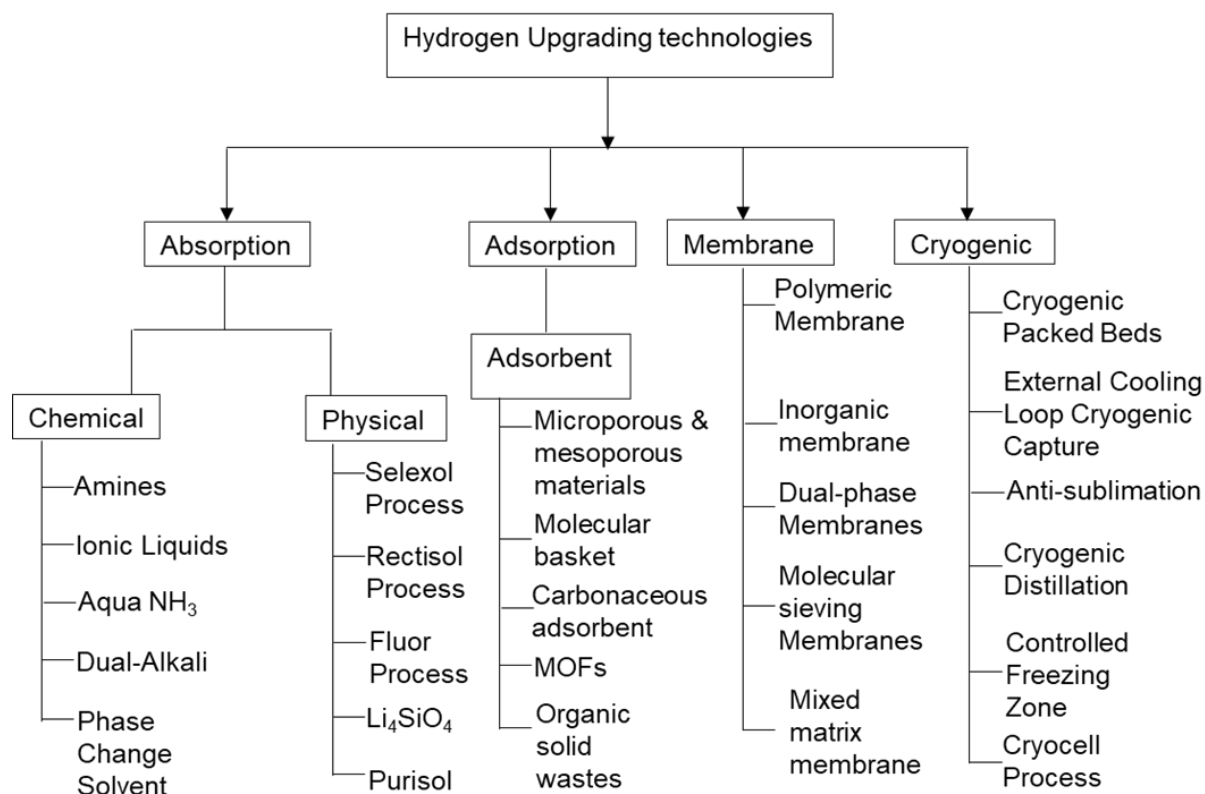


Figure 2.5: CO₂ separation technologies

2.4.1 Absorption Methods of CO₂ Separation

Absorption is a widely used method for CO₂ separation from gas streams. The process involves the uptake of CO₂ by a solvent or absorbent, either through physical or chemical interactions. The choice between physical and chemical absorption depends on the specific application, the nature of the gas stream, and economic considerations. The advantages of using this method include a fast response, strong absorption capacity, and convenient application. However, challenges faced in its use include equipment corrosion, high regeneration energy consumption, and elevated operating costs. The energy consumption ranges from 1.83–4.0 GJ/t CO₂ (102–105).

2.4.2 Chemical Absorption

Chemical absorption is a method wherein CO₂ interacts with a solvent, leading to a chemical bond formation. This bond formation ensures a stable capture of CO₂, making it a reliable method for gas separation. The process is typically characterised by its reversibility. By applying heat or changing conditions, the absorbent can be regenerated, releasing the captured CO₂ in a concentrated form. This method's effectiveness is influenced by factors like solvent choice, temperature, and pressure. The ability to recycle the solvent makes it economically appealing for large-scale operations (106). This method is particularly suitable for post-combustion capture. Solvents or the absorbent includes Amines, ionic liquids, phase change solvents, Dual-Alkali and Aqua NH₃.

1. **Amines:** Amines, such as MEA, diethanol amine (DEA), and N-methyldiethanolamine (MDEA), are commonly used solvents for CO₂ capture. MEA has been employed in the natural gas industry for over 60 years and can achieve a CO₂ recovery rate of 98% (107). However, the stability of amines and the energy consumption for the stripping process have room for improvement.
2. **Ionic Liquids (ILs):** ILs are salts in a liquid state and have emerged as potential solvents for CO₂ capture either by chemical absorption process or physical absorption process because of their low volatility and high CO₂ solubility. They can selectively capture CO₂ from gas mixtures, offering potential advantages in terms of energy efficiency and reduced solvent losses (108). Riva et al. reported an energy requirement of 1.4 GJ/ton of captured CO₂ using AHA ILs (53).
3. **Phase Change Solvents:** This set of solvents, distinct from conventional solvents, transition from a homogeneous to a heterogeneous system upon triggers like CO₂ absorption or temperature changes, resulting in separate CO₂-lean and CO₂-enriched phases (109). These solvents undergo phase separation when CO₂ reacts with the solute

or post-reaction temperature rises. The CO₂-rich phase, which can be liquid or solid, requires regeneration, offering energy-saving benefits. Specifically, CO₂-triggered biphasic solvents have lower heat requirements for regeneration (110). Recent studies indicate that by adjusting solvent composition, particularly with blended amines, the phase separation temperature can be optimised, though predicting this temperature remains complex due to varied species formed during CO₂ absorption (110).

4. Dual-Alkali System (DAS): This process is a sophisticated CO₂ absorption technique that employs two distinct alkali substances. The primary advantage of this method is its enhanced absorption efficiency, achieved by leveraging the unique properties of both alkalis. Additionally, by using two alkalis, the solvent's degradation rate is significantly reduced, prolonging its usability, and reducing operational costs. This method is particularly beneficial in scenarios where high CO₂ capture rates are essential, and solvent longevity is a concern. The strategic combination of alkalis ensures optimal performance and sustainability (111). As reported by Yang et al., their study found that the energy demand for K₂CO₃ regeneration for CO₂ capture averaged 0.82 GJ/ton of CO₂ under steady-state conditions (41) as shown on **Table 2.3**.

5. Aqua Ammonia (NH₃): The Aqua Ammonia Process, which uses aqueous ammonia NH₃ as a CO₂ sorbent, has been recognised for its potential in CO₂ capture (112). This process has demonstrated a CO₂ removal efficiency as high as 99%, with an absorption capacity exceeding 1.0 kg CO₂/kg NH₃. In comparison, the maximum CO₂ removal efficiency and absorption capacity for the MEA solvent were 94% and 0.40 kg CO₂/kg MEA, respectively. The temperature rises in the NH₃ scrubbing process is less than that in the MEA scrubbing, indicating a lower heat requirement for regeneration in the NH₃ process. This translates to significant energy savings, with the NH₃ process potentially saving up to 60% of the energy compared to the MEA process. Furthermore, the

absorption capacity of NH_3 was found to be 2.4–3.2 times higher than MEA, making NH_3 a more economical choice for CO_2 scrubbing (113).

- 6. Metal Oxides:** Metal oxides like CaO and MgO retain high adsorption capacities at temperatures above 300°C . The operation involves a carbonation-calcination cycle (97).

2.4.2.1 Physical Absorption

This is a method where CO_2 is captured by being physically dissolved in a solvent, akin to how a gas dissolves in a liquid under pressure. This process is governed by Henry's Law, implying that the solubility of CO_2 in the solvent is temperature and pressure dependent. In physical absorption, there's no chemical reaction between the CO_2 and the solvent. Instead, the solubility of CO_2 within the solvents depends on the partial pressure and the temperature of the feed gas. Higher CO_2 partial pressures and lower temperatures favour the solubility of CO_2 in the solvents. The solvents used in this process are then regenerated by either heating or reducing pressure. The interaction between CO_2 and the absorbent in physical absorption is relatively weak compared to chemical solvents, which results in a decreased energy requirement for regeneration (94). This process includes:

- 1. Selexol:** This process uses a solvent to physically absorb CO_2 . It's commonly used in gas processing plants to remove CO_2 and sulphur compounds.
- 2. Rectisol:** This method uses cold methanol as the solvent to wash out the acid gases from synthesis gas.
- 3. Fluor Process:** This process employs proprietary solvents developed by the Fluor Corporation for CO_2 capture.
- 4. Lithium silicate (Li_4SiO_4):** This offers potential for CO_2 capture in energy processes, but traditional preparation shows suboptimal absorption. Research focuses on improving its capacity and stability (114).

5. **Purisol:** This process uses an organic solvent, typically N-methyl-2-pyrrolidone, to absorb CO₂.

Table 2.3: Energy requirements for CO₂ separation using both chemical and physical absorption methods.

Method/Solvent	Energy Requirement	
	(GJ/ton of captured CO ₂)	Reference
Amines-based (Chemical)	4.2	(36)
Aqua ammonia (Chemical)	4.07	(40)
[bmim][Ac] (Chemical)	3.2	(111)
Phase change solvents	2.33	(115)
ILs (Chemical)	1.4	(53)
ILs (Physical)	1.4	(54)
Rectisol (Physical)	0.925	(116)
Dual-alkali system (Chemical)	0.82	(41)
Selexol (Physical)	0.34 - 0.57	(117,118)

2.4.3 Adsorption Methods of CO₂ Separation

Adsorption is a method used for CO₂ separation where CO₂ molecules adhere to the surface of a material, known as an adsorbent. This process relies on porous solid adsorbents like zeolites and activated carbon. Unlike absorption where CO₂ dissolves in a solvent, adsorption may not involve chemical reactions between the adsorbent and CO₂. The efficiency of this separation depends on the adsorbent's affinity for CO₂. Two primary techniques in this method are pressure swing and temperature swing processes (107). After saturation, the adsorbent is regenerated, often involving changes in pressure or temperature, to release the captured CO₂, preparing it for another cycle (93). One significant advantage of adsorption over absorption is its reduced energy intensity, facilitating easier adsorbent recovery (119). Traditional adsorption methods typically consume between 1-3 GJ ton⁻¹ CO₂ (42).

Adsorption can be categorised into two main types based on the adsorbent used:

1. **Physical adsorption (physisorption):** Uses adsorbents like activated carbon and zeolites to establish van der Waals interaction (97) with CO₂.
2. **Chemical adsorption (chemisorption):** Employs adsorbent materials such as calcium carbonate, calcium oxide, and magnesium oxide to establish covalent bonding interactions (97) with CO₂.

2.4.3.1 Adsorbents

1. **Microporous and Mesoporous Materials:** Zeolites are among the most widely reported physical adsorbents for CO₂ capture (97). They are primarily used for commercial hydrogen production involving H₂/CO₂ separation using pressure swing adsorption (97).
2. **Molecular Basket:** This is a concept where mesoporous materials like MCM-41 are combined with polyethyleneimine (PEI) to create a highly selective and high-capacity CO₂ adsorbent. This molecular basket can selectively capture CO₂ from simulated flue gas and natural gas-fired and coal-fired boiler flue gas (107).
3. **Carbonaceous Adsorbents:** Studies on activated carbon, charcoal, and virgin coal have mainly focused on high-pressure CO₂ capture applications. Few studies have investigated their feasibility for low-pressure flue gas applications using vacuum or temperature swing regeneration approaches (97).
4. **Lithium Compounds:** Lithium zirconate (Li₂ ZrO₃) has been investigated as a HT CO₂ absorbent due to its favourable CO₂ sorption characteristics (107).
5. **Solid waste and Organic Solids:** Solid waste-derived materials are emerging as promising sorbents for CO₂ capture. The utilisation of these materials aligns with cleaner production concepts, offering competitive adsorbent processing costs while

simultaneously reducing waste pollution (120). Non-porous self-assembled p-tert-butylcalix(4)arene organic solids have been considered for CO₂ capture (97).

6. **Metal-organic frameworks (MOFs):** MOFs are crystalline porous solids made of metal oxide centres connected by organic linkers. Their unique structure, high surface area, and tunability make them ideal for CO₂ capture, outperforming other materials like zeolites and activated carbons. MOFs have been extensively researched for CO₂ sequestration and conversion (121,122).
7. **Polymeric adsorbents:** They are particularly porous organic polymers such as hyper-cross-linked polymers (HCPs), covalent organic frameworks (COFs), and polyethyleneimine-modified materials, demonstrate effective CO₂ capture with capacities ranging from 3 to 6 mmol/g. Their application spans industrial settings, leveraging waste polymers for dual environmental benefits (123).

2.4.4 Cryogenic Technology for CO₂ Capture

Cryogenic CO₂ Capture (CCC) is an innovative method for capturing carbon dioxide (CO₂) from post-combustion flue gases. The technology hinges on the principle that different gas components condense or liquefy at varying temperatures. In the context of CO₂ capture, the gas mixture is cooled to a point where CO₂ transitions into a liquid or solid phase, facilitating its separation from other gases (124).

The CCC process comprises several steps which include:

1. **Pre-cooling:** Initial cooling using conventional refrigeration techniques.
2. **CO₂ condensation:** Further cooling to induce CO₂ liquefaction or solidification.
3. **Separation:** Extracting the condensed or solidified CO₂ from the gas stream.
4. **Regeneration:** Warming the captured CO₂ to release it as a pure gas.

One of the standout benefits of cryogenic technology is its potential to achieve high CO₂ purity levels, often surpassing 99% (125). Moreover, the solid CO₂ product has a denser and more compact form than its gaseous and liquid states, optimising transportation efficiency. However, challenges persist, including the energy-intensive nature of the process and the high costs associated with cryogenic equipment (125). Despite these hurdles, the technology holds promise, especially for large-scale applications like coal-fired power plants exceeding 200 MW. Notably, this method can capture CO₂ without chemical solvents, eliminating the energy-intensive regeneration step seen in solvent-based processes (43). A primary concern with this technology is the substantial energy required to achieve the necessary cryogenic conditions. The energy consumption for this method can range from 0.395–3.4 GJ/t CO₂, depending on the specific technique employed (43). By 2030, projections suggest that China's CO₂ capture cost using this technology will be between 13–57\$/t, and by 2060, it could decrease to 3–19\$/t. When considering both fixed and operating costs, the total abatement cost is estimated around 65\$/t CO₂ (124).

To mitigate the high energy demands, researchers have proposed innovative energy-saving processes, such as the post-expansion and pre-cooled methods. These strategies focus on integrating pressure recovery and utilising cold energy from residual gas, aiming to optimise energy consumption (125). For instance, a design by Clodic and Younes (2002) (126) involves a cryogenic CO₂ capture process where CO₂ solidifies on a heat exchanger's surface. This system leverages controlled frosting and defrosting stages, capitalising on the latent heat of CO₂ during its phase transition (125).

In the broader context of CO₂ capture, energy consumption is pivotal for determining a process's feasibility and efficiency. This encompasses thermal energy for solvent regeneration, electrical energy for equipment operation, and energy for compressing captured CO₂ for

transport and storage. Specifically, for cryogenic methods, cooling is a significant energy demand, essential for achieving efficient CO₂ absorption.

Two primary systems are employed based on the phase of CO₂ post-separation (127):

- **Conventional V-L Separation:** Utilises varying boiling points of CO₂ and other gases. It's more energy-intensive due to high pressures and the need to prevent solid CO₂ formation. This is basically Cryogenic Distillation.
- **Unconventional V-S Separation:** More energy-efficient, it achieves desublimation conditions where CO₂ forms a solid, requiring contact with a cold medium. This includes Cryogenic Packed Beds, External Cooling Loop Cryogenic Capture, Anti-sublimation, Controlled Freezing Zone and Cryocell Process.

2.4.4.1 Cryogenic Packed Beds

Cryogenic Packed Beds, categorised under Unconventional V-S Separation, is an innovative technology for CO₂ capture. This method employs packed beds filled with cold bed material that acts as a heat transfer surface. Cryogenically cooled nitrogen gas pre-cools the bed material. When the flue gas, rich in CO₂, is introduced, it is cooled by the bed material, causing the CO₂ to desublimate and form a frost on the bed material's surface as shown on **Figure 2.6**. This approach leverages cryogenic principles to separate and capture carbon dioxide from gas streams, resulting in the condensation or solidification of CO₂. The structured bed, filled with specific materials, enhances the separation process's efficiency (43,127). The energy consumption is in the range of 2.4 – 5.2 GJ/tCO₂ (43,128).

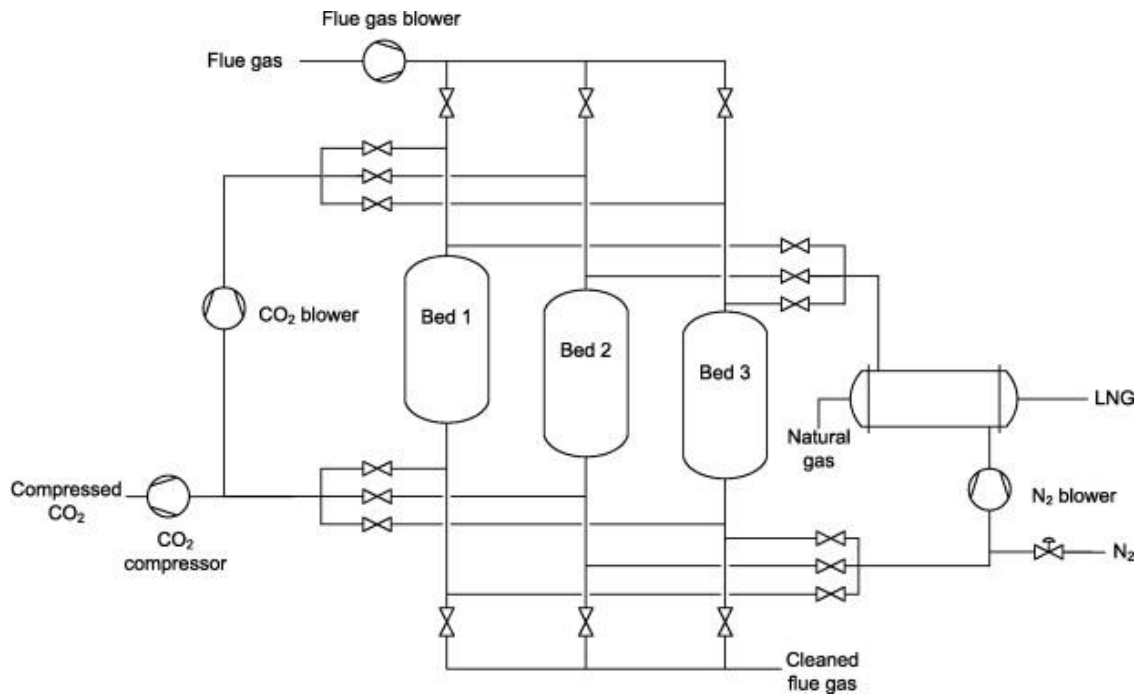


Figure 2.6: The flow process diagram of a cryogenic packed bed for CO₂ capture from (129).

2.4.4.2 External Cooling Looping Cryogenic Capture (ECL)

External Cooling Looping Cryogenic Capture (ECL) is a cryogenic process categorised under Unconventional V-S Separation and that leverages the "waste cold energy" from industrial sources, notably liquefied natural gas (LNG), for CO₂ separation. It employs heat exchange to desublime CO₂ frost. The flue gas is initially dehydrated, then passed through a heat exchanger and mixed with a contact liquid, resulting in the desublimation of 99% of the CO₂ from the gas phase (127) as shown in **Figure 2.7**.

The ECL system operates through five primary stages (130):

1. Drying and cooling the flue gas.
2. Compressing the gas and cooling it to just above CO₂'s freezing point.
3. Expanding the gas for further cooling.
4. Precipitating a portion of the CO₂, the form of which depends on the final temperature.

5. Pressurising and reheating the CO₂ alongside the "residual flue gas" using incoming gases.

In this process, CO₂ is collected in its liquid phase, while a nitrogen-rich stream is released. A distinctive feature of the ECL is its capacity to store energy as LNG (131), enabling the mitigation of energy losses from CO₂ removal. The system uses stored refrigerant during peak demand, transferring the reduced parasitic load to the grid, and regenerates the refrigerant during off-peak times (132). Its "rapid-load-change capability" ensures compatibility with traditional power generation systems (130).

Various studies have reported differing energy penalties for the ECL. Song et al. noted an energy penalty of 5.04 GJ/ton CO₂ (43), Jensen provided values of 1.67, 0.74, and 0.92 GJ/ton CO₂ in separate studies (133), and Ebrahimzadeh et al. reported an energy penalty of 0.98 GJ/ton CO₂ (134).

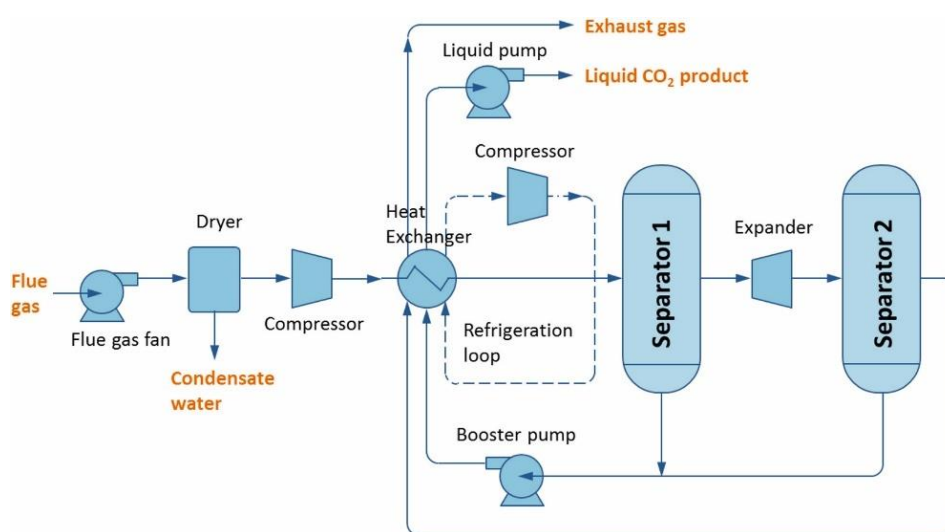


Figure 2.7: The flow process diagram of an ECL cryogenic capture of CO₂ from [60].

2.4.4.3 Anti-Sublimation CO₂ capture

The Anti-Sublimation CO₂ capture process, commonly referred to as AnSU, is an innovative carbon capture method introduced by Clodic and Younes (126). This technology capitalises on

the principle of AnSU, capturing CO₂ in its solid state directly from flue gases. The AnSU process is structured into five primary stages as shown in **Figure 2.8**:

1. Flue Gas Clean-up and Cooling: The flue gas undergoes cleaning, moisture removal, and cooling to a temperature of -40°C .
2. Heat Exchange: Heat is exchanged between CO₂-rich and CO₂-poor flue gases.
3. Refrigeration Integrated Cascade: This stage ensures the maintenance of the required temperatures.
4. CO₂ Freezing Heat Exchange: CO₂ solidifies and is captured.
5. CO₂ Recovery: Solid CO₂ is retrieved for subsequent use or storage.

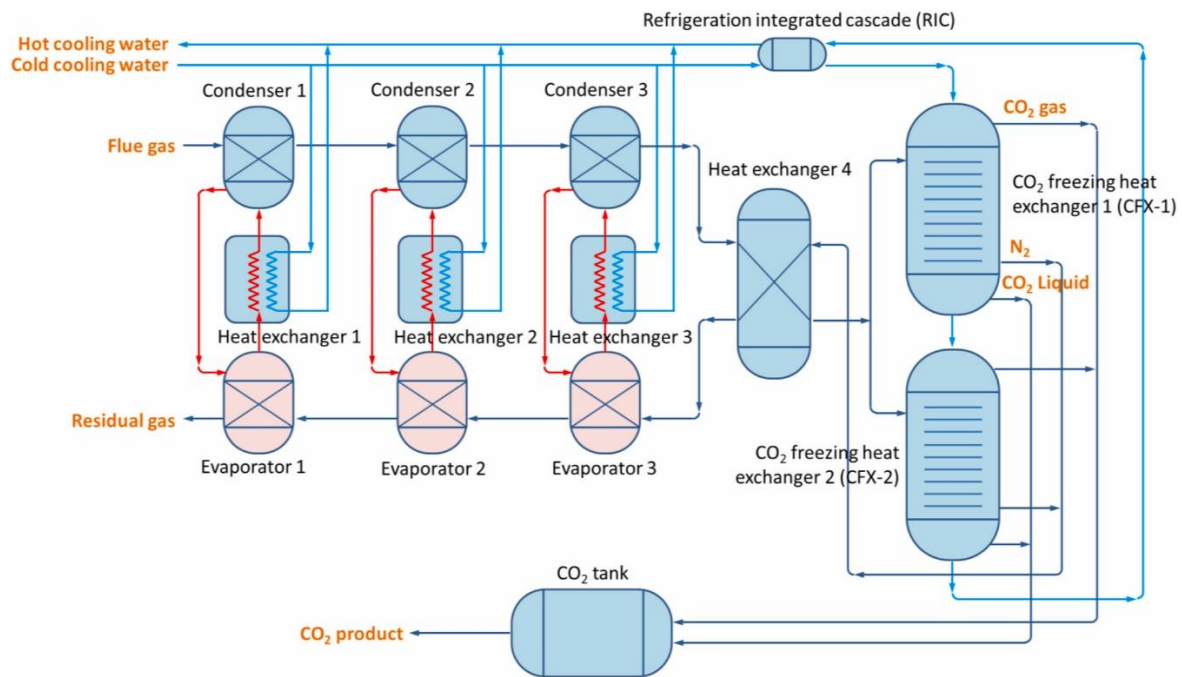


Figure 2.8: The flow process diagram of an AnSU cryogenic capture of CO₂ from (43).

This method was effectively demonstrated on a 660 MWe boiler, achieving a CO₂ concentration of 15.47% under conditions of 60°C and 120 kPa (135).

A significant advantage of the AnSU process is its energy efficiency. Its energy penalty ranges from 3.8–7.2% of the power plant's efficiency (136), making it more energy-efficient than the MEA absorption process, which results in about a 14% efficiency decrease (136). Another

benefit is the recovery of the heat of fusion during CO₂ defrosting on the heat exchanger surface, which is then used to cool the refrigerant blend before evaporation (126).

2.4.4.4 Cryogenic Distillation

Cryogenic distillation is a well-established separation technology, predominantly used in the purification of natural gases. As proposed by Holmes and Ryan (137), the process involves cooling the feed gas using a pre-cooler and a heat exchanger. Once cooled, the gas is directed to a distillation column equipped with vapor-liquid contact devices, such as trays or packing materials. The distillation column separates the gas into two primary streams: the top product, which is mainly methane, and the bottom product, which is condensed CO₂. A portion of the CO₂-rich stream is recycled through a reboiler to provide vaporisation heat, while the rest undergoes further separation to extract purified CO₂. This process is illustrated in **Figure 2.9**.

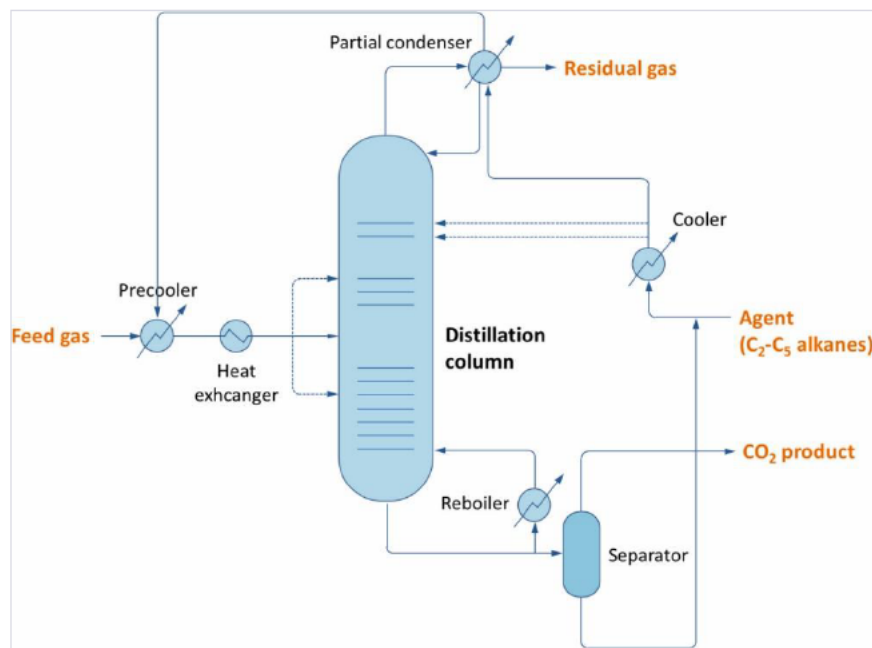


Figure 2.9: The flow process diagram of a cryogenic distillation capture of CO₂ from (43).

One of the most significant challenges of cryogenic distillation is its high energy consumption. It is reported that the energy demands of this process can account for over half of the plant's operating costs (112,134,138,139). This high energy requirement is a critical factor that can

impact the feasibility and economic viability of the technology. Berstad et al. quantified this by reporting an energy penalty of 1.9 MJe/kg CO₂ when removing CO₂ to an LNG specification of 50 ppm from a starting concentration of 50.6% CO₂ (140).

To address the energy-intensive nature of cryogenic distillation, several energy-efficient solutions have been proposed. These solutions leverage process integration and intensification techniques, such as cyclic distillation, heat-integrated distillation columns, reactive distillation, and thermally coupled columns (141,142). Notably, Maqsood et al. (143–145), introduced an intensified side-mounted and integrated switched cryogenic network configuration for CO₂ separation from natural gas. Their research findings indicated a significant reduction in energy requirements, methane loss, and size requirements when using these intensified hybrid cryogenic distillation networks. Impressively, the overall profit surged by 69.24% with the optimisation of this intensified cryogenic network (146).

2.4.4.5 Stirling coolers

The free piston Stirling coolers (FPSCs), emerges as a promising technique for efficient CO₂ capture from flue gas. This method is strategically divided into three distinct units to ensure moisture removal, CO₂ solidification, and its subsequent storage. These includes **Figure 2.10:**

- 1. Cryogenic unit 1 (C-1):** In this initial phase, the flue gas is chilled by FPSC-1. This action condenses the moisture present in the feed gas into water, which is then drained to prevent any clogging. The resultant dry flue gas is pre-chilled, setting the stage for CO₂ anti-sublimation in the subsequent unit.
- 2. Cryogenic unit 2 (C-2):** Here, FPSC-2 (i.e., the freezing zone) establishes the cryogenic conditions, cooling the flue gas to temperatures below -100°C. As the gas stream interacts with the cold head, CO₂ solidifies, forming dry ice that frosts onto the cold head's surface.

3. **Cryogenic unit 3 (C-3):** In this final unit, a motor-driven scraping rod is employed to detach the deposited CO₂ from the cold head. The captured CO₂ is then stored within C-3, where FPSC-3 maintains a low temperature, ensuring the dry ice remains solid and doesn't revert to its gaseous state.

A comprehensive representation of this cryogenic process can be found in **Figure 2.10**, which delineates the entire procedure and its segmentation into the three cryogenic units.

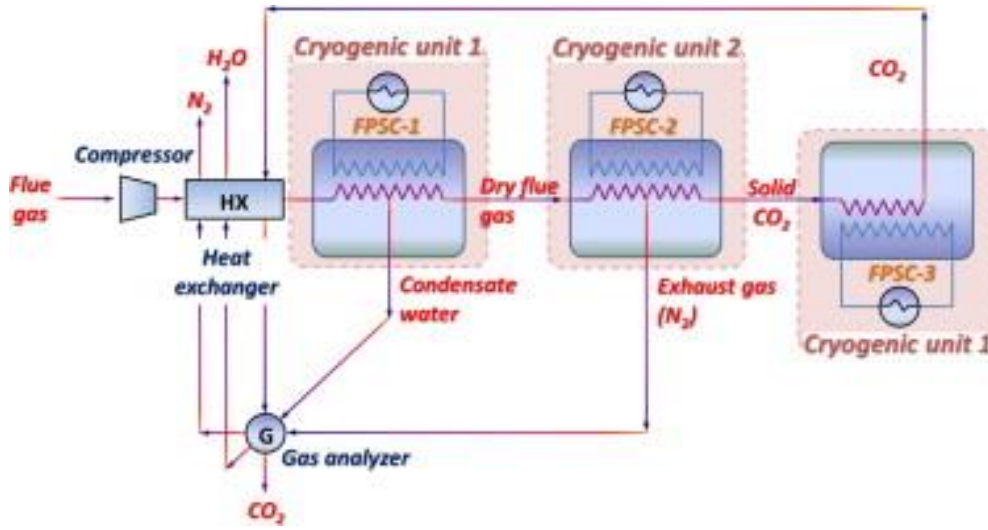


Figure 2.10: The flow process diagram of Stirling coolers cryogenic capture of CO₂ from (147).

The energy consumption (EC) of the system per unit mass of captured CO₂ is given by the Equation (2.1):

$$EC = \frac{VI}{\left(\frac{\dot{f}_{in} Y_{CO_2, in} P_{in}}{T_{in}} \right) - \left(\frac{\dot{f}_{out} Y_{CO_2} P_{out}}{T_{out}} \right)} \cdot \frac{nR}{M_{CO_2}} \quad (2.1)$$

Where, V and I are voltage and current in the system respectively, $\dot{f}_{in}$ and $\dot{f}_{out}$ are volumetric flow rates of the gas mixture at the inlet and outlet.

y is the mole fraction of CO₂ in the gas mixture, P and T are pressure and temperature at the inlet and outlet. M_{CO_2} is the molar mass of CO₂.

2.4.4.6 Cryocell Process

CryoCell technology, developed by Cool Energy Ltd. and tested in collaboration with partners like Shell Global Solutions in Western Australia, offers a unique approach to CO₂ capture (148). The process, as illustrated in **Figure 2.11**, is reminiscent of the ECL method, with both technologies relying on cooling mechanisms to separate CO₂ from flue gas (FG).

The CryoCell process begins with the dehydration of the feed gas to ensure it meets low water specifications, a crucial step to facilitate the subsequent cryogenic operations. Once dried, the gas undergoes heat exchange with treated gas and cold CO₂, cooling the CO₂ to its freezing point. This cooled CO₂ is then expanded using a Joule-Thomson (J-T) valve, resulting in a three-phase mixture. Within the CryoCell separator, solid CO₂ settles at the bottom and is subsequently melted by a heater, allowing for its separation in a liquid phase. The remaining gas is compressed to meet sale-gas specifications, while the liquid CO₂ is pumped to the desired disposal pressure.

One of the standouts features of the CryoCell technology is its energy efficiency, especially at higher CO₂ concentrations exceeding 20%. However, it's worth noting that the inclusion of compressors in the process can increase the energy consumption cost (ECC) (43). For CO₂ concentrations ranging between 20% to 35%, the system achieves a capture efficiency of 34% (148). This indicates that while the technology is promising, its efficiency can vary based on the initial CO₂ concentration in the flue gases. However, the increased energy consumption due to the use of compressors and the variable efficiency based on CO₂ concentrations are areas that might benefit from further optimisation. Future research and development in this domain could potentially enhance the technology's efficiency and make it a more viable option for large-scale CO₂ capture.

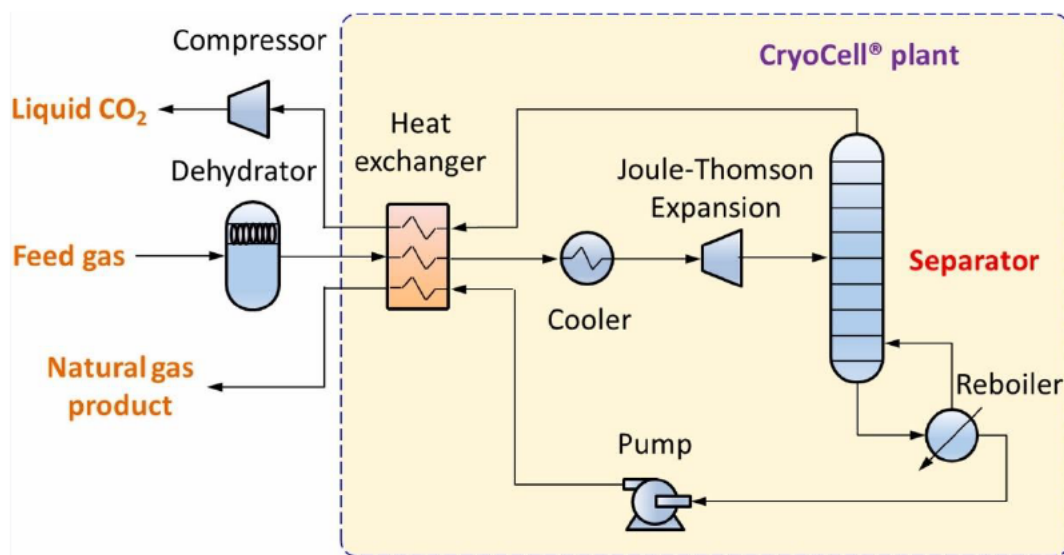


Figure 2.11: The flow process diagram of controlled freezing zone cryogenic capture of CO₂ from (43)

2.4.4.7 Controlled Freezing Zone

The Controlled Freeze Zone (CFZ) technology, introduced by ExxonMobil in 1983, is a cryogenic distillation method specifically designed to purify natural gas by removing impurities, including CO₂ (149). The technology's core mechanism involves the freezing and subsequent melting of CO₂ within a specialised chamber situated in the midst of a distillation column, as depicted in **Figure 2.13**. The distillation column is divided into three main sections: the upper and lower sections, which are conventional packed beds, and a unique middle section. This middle section comprises spray nozzles, a freeze zone, and melting trays. As dehydrated and cooled natural gas is fed into the upper section, CH₄ vaporises due to the increased residual CO₂ concentration. In the middle section, liquid CO₂ is sprayed, leading to its solidification. The solid CO₂ is then collected on melt trays, where it's melted into a liquid and subsequently removed from the column's bottom section. The end products are high-purity liquid CO₂ and high-purity CH₄. Under optimal conditions, the process can achieve a remarkable capture rate of 95.20% CO₂, with an energy consumption of just 0.52 MJ/kg of captured CO₂ (147).

ExxonMobil's commercial demonstration of the CFZ technology in Wyoming, USA, has shown the potential economic benefits of the method (150). Notably, the captured CO₂ from this facility is repurposed for enhanced oil recovery (EOR), which can bolster the economic viability of sour natural gas extraction. Furthermore, Exxon asserts that the CFZ technology offers a more cost-effective solution in terms of capital costs, being 10–27% lower than other gas treatment alternatives like Selexol and Ryan-Holmes (151). However, it's essential to note that the CFZ technology might not be as economical when the gas contains a significant concentration of ethane or higher hydrocarbons (152).

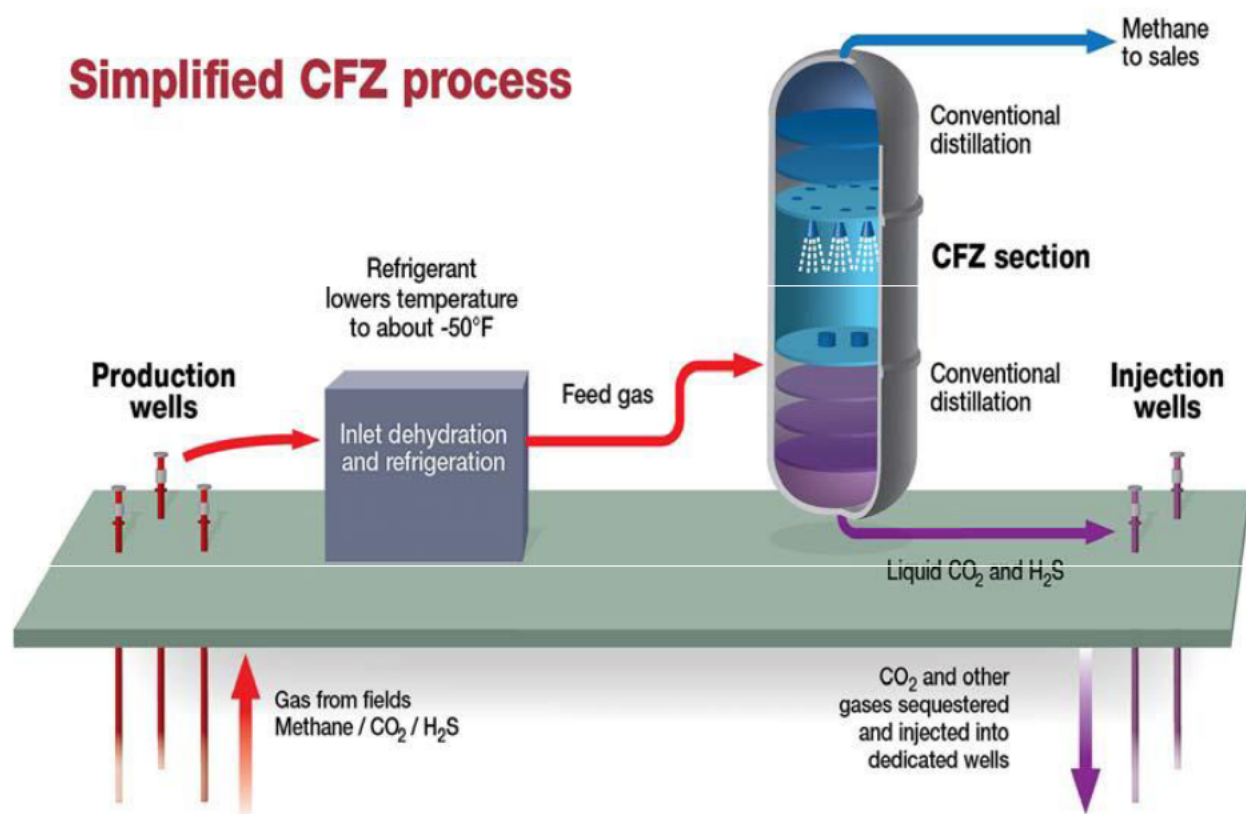


Figure 2.12: The flow process diagram of controlled freezing zone cryogenic capture of CO₂ from (150).

2.4.5 Membrane Technologies for CO₂ capture

Membrane technologies have emerged as a promising avenue for CO₂ capture. At its core, a membrane acts as a selective barrier, allowing certain components to pass through more readily than others. The "permeate" is the portion of the feed that traverses the membrane, while the "retentate" remains behind. The driving force behind this separation is typically the difference in partial pressures across the membrane, and in some processes, compression power may be required (86). **Figure 2.13** illustrates a two-stage membrane separation strategy, where a portion of the permeate is used as a sweep to enhance the separation process (153).

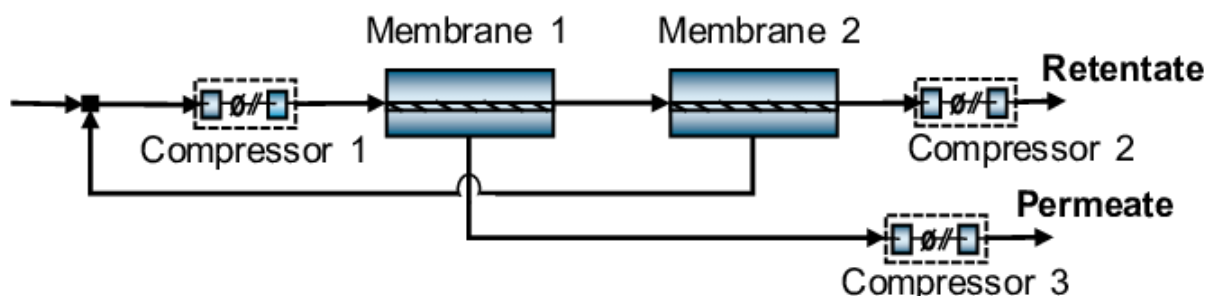


Figure 2.13: The flow process diagram of a membrane technology for CO₂ capture from (154).

Membrane technologies are lauded for their energy efficiency, especially when compared to traditional separation techniques such as distillation or evaporation, which involve phase changes (155). By utilising the pressure of the feed gas, membrane separation often results in energy consumption figures that are lower than these conventional methods. In specific configurations, CO₂ can be captured with an energy consumption of less than 0.5 GJ ton⁻¹ CO₂ (42). However, a particular study using polyethylene oxide (PEO) and Pebax 1657 polymer membranes noted an energy consumption of 2.88 GJ ton⁻¹ CO₂, achieving a CO₂ recovery rate of 75.2% and a purity of 96.7% (42). However, most of the membrane technology has an energy consumption in the range of 1.1–1.9 GJ/t CO₂ (44–47). Thus, the efficiency largely depends on the specific membrane technology employed for separation.

Membrane technologies offer several advantages, including simplicity, energy efficiency, and eco-friendliness (156). They are particularly suitable for applications where the primary objective is hydrogen purification for combustion, and their efficiency can be further enhanced by integrating adsorption or cooling processes (42). However, there are challenges. Membranes have strict temperature requirements, with structures deteriorating rapidly if flue gas temperatures exceed 100 °C (157). They are also sensitive to corrosive gases, necessitating pre-treatment. Maintaining membrane performance over extended periods is challenging, with many membranes lacking resilience under industrial conditions (158). Several types of membranes have been explored for CO₂ capture and this includes Polymeric membrane, mixed matrix membrane, porous inorganic membranes, dual-phase membrane and molecular sieving membrane (86).

2.4.5.1 Polymeric Membrane

Polymeric membranes have emerged as a promising avenue for CO₂ capture, boasting distinct advantages and mechanisms for gas separation. They primarily operate based on two mechanisms: solution-diffusion and facilitated transport (86).

1. **Solution-Diffusion Mechanism:** This mechanism achieves separation by capitalising on the difference in the amount of the penetrant that dissolves in the polymer and/or the rate at which the penetrant diffuses through the polymer (159).
2. **Facilitated Transport Mechanism:** This approach enhances mass transfer through the reversible reaction between the penetrant and reactive carriers (159).

Emerging polymeric membrane materials for CO₂/gas separation are classified based on their interaction with CO₂ and their polymer architecture. This classification encompasses ether oxygen-rich polymers, polymeric ILs, perfluoropolymers, thermally rearranged polymers, glassy polymers with iptycene as a foundational block, other non-reactive polymers, and

facilitated transport polymer membranes (160). Advantages of using the polymeric membrane includes cost-effectiveness, high density of packaging and ease of processing. Furthermore, a variety of polymers, including polyimides, polyamides, block copolymers, and hydrophilic polymers, have been explored for membrane fabrication (161). Some polymers, such as poly (amide-b-ether) — commercially known as Pebax® — are already available in the market, underscoring their industrial feasibility (162). However, it's worth noting that despite their myriad advantages, polymeric membranes may not be ideal for harsh chemical environments and elevated temperatures, especially in settings like refineries and petrochemical plants. The choice of polymer and its architecture are pivotal in determining the membrane's efficiency and selectivity.

2.4.5.2 Mixed Matrix Membranes:

Mixed Matrix Membranes (MMMs) represent an innovative approach to gas separation, designed to address the inherent limitations of traditional polymer membranes. Traditional polymer membranes often grapple with a permeability-selectivity trade-off, which hinders their efficiency. MMMs, however, are constructed by integrating two or more distinct materials with varying properties. Typically, one material, usually a polymer, forms a continuous phase termed the matrix, while another material, either inorganic or organic, forms a dispersed phase, known as the filler. The combination of these two components, each with its unique transport properties, allows MMMs to potentially transcend the constraints of traditional polymer membranes in gas separation applications (157).

The polymer offers ease of fabrication, scalability, and tunable membrane configuration, while the inorganic filler provides high selectivity, thermal and chemical stability, and tunable pore size (163). Zeolite imidazolate frameworks (ZIFs) are frequently utilised as fillers in MMMs due to their adjustable pore channels, unsaturated sites, and ease of functionalisation (164).

Other inorganic fillers can include carbon molecular sieves (CMS), zeolites, and carbon nanotubes (CNTs) (165). MMMs typically demand lower energy due to their enhanced separation performance over native polymer membranes. This energy efficiency is attributed to the synergistic combination of the polymer matrix and the inorganic filler, which together optimise the membrane's separation capabilities (156).

2.4.5.3 Inorganic Membranes

Selective for CO₂ either by surface diffusion or capillary condensation. They have high separation efficiency but are costly and can have defects (86).

2.4.5.4 Dual-Phase Membranes

Dual-phase membranes comprise a molten carbonate phase and metal or ceramic phase, suitable for HT operations (86).

2.4.5.5 Molecular Sieving Membranes

Molecular sieving membranes constructed from metal-organic framework nanosheets (42).

2.5 CO₂ Infrastructure and Transport

After CO₂ is captured, it must be transported to storage sites as shown in **Figure 2.15**. This process requires a large-scale infrastructure to accommodate the vast volumes involved (166). CO₂ is transported through dedicated pipelines and ships and is eventually stored in geological reservoirs. These reservoirs can be depleted oil and gas fields or saline aquifers (167). CO₂ can be transported in various phases: gaseous, liquid, or occasionally solid. Feasible transportation alternatives include pipelines (both onshore and offshore), water carriers (offshore), and combinations thereof.

CO₂ from capture



Figure 2.14: The chain diagram of CO₂ transport from (167)

Offshore CO₂ transport primarily utilises two methods: pipeline and ship transport. Both have been explored in various projects. For example, the Green Hydrogen project, which is currently paused, contemplated using ships to transport CO₂ from the Netherlands to mature oil fields in Denmark (168). Despite this, there's limited experience with offshore CO₂ pipeline and ship transport. Presently, only the Snøhvit pipeline, spanning 150km and transporting roughly 0.7 MtCO₂ annually, exists offshore (169). In terms of shipping, approximately 3 MtCO₂ is transported annually for industries like food using small-scale ships of 800–1200 m³ capacity (170,171). These figures are modest when compared to the projected global capture and storage of 226 MtCO₂/y by 2025, as per the 2°C scenario of the International Energy Agency (172).

Studies by Roussanaly et al., (173), Jung et al. (174), and Svensson et al. (175) have evaluated both transport modes. Their findings suggest that pipelines are more cost-effective for transporting large CO₂ quantities (>5 MtCO₂/y) over short distances (<200 km). In contrast, ships are more economical over longer distances (>1000 km). The break-even distance is estimated at roughly 700 km for transporting 6.2 MtCO₂ annually (176), and this distance increases with higher mass flows (177,178). A notable difference between the two transport modes is their cost structure. Pipelines predominantly consist of capital expenditures (CAPEX), making up 75-95% of the total costs. In contrast, ships mainly comprise operational expenditures (OPEX), accounting for 60-80% of the costs (168). This CAPEX-OPEX structure suggests that ships might have a financial edge over pipelines, especially if the duration of a CCS project is shorter than expected or uncertain. Furthermore, ships offer flexibility. If a storage reservoir's capacity is overestimated, ships can easily reroute to another storage site.

Pipelines, however, face higher rerouting costs, often necessitating the construction of additional sections or entirely new pipelines.

In conclusion, while the transportation of CO₂ is technically feasible through various means, economic considerations often dictate the choice. Onshore, pipelines are preferred due to their cost-effectiveness and ability to handle vast quantities of CO₂. Offshore, the choice between water carriers and pipelines is more balanced, with each option presenting its unique set of advantages and challenges.

2.6 Regulatory and Policy Framework

Regulation is instrumental in guiding the adoption and implementation of CCS technologies. It bridges the gap between the scientific consensus on GHG emission reductions and their practical realisation. As Bowen et al. (179) highlight, achieving stable atmospheric GHG concentrations demands significant technological and institutional shifts.

2.6.1 Current Regulatory Environment: Global and Regional Perspectives

The global regulatory landscape for CCS presents both challenges and opportunities. A major hurdle is the nascent regulatory and liability frameworks (179). Globally, there's an acknowledgment of the need to align with the Paris Agreement's decarbonisation goals. The European Union, for instance, has set ambitious carbon reduction targets such as a reduction of 80-95% by 2050, based on 1990 levels, underpinned by Directive 2009/31/EC, which focuses on CCS development (180). China, bound by the London Protocol, must ensure its domestic regulations are in sync with international standards. Meanwhile, the Middle East, especially the GCC region, faces challenges due to the absence of a unified regulatory framework, despite its significant carbon capture, usage and storage (CCUS) potential (180).

2.6.2 Policies on Supporting and Hindering Factors

Policies play a crucial role in either promoting or inhibiting CCS adoption. Policymakers need to be cautious of incumbents resisting change and should foster a sense of urgency through clear policy timelines (179). Collaborations with firms having positive risk experiences, transparent subsidisation processes, and higher carbon prices can further encourage CCS investments (179). Additionally, integrating CCUS into climate mitigation plans and ensuring alignment with international laws is essential (180).

2.6.3 Future of Regulatory Landscape: Predictions and Recommendations

The regulatory landscape for CCS is set for transformation. Policymakers can prioritise disruptive projects over sustaining ones and reconsider the current emphasis on post-combustion CCS. Frances et al. (179) advocate for public research spending on universally deployable CCS technologies and knowledge sharing to hasten the learning curve. Rissman et al. (181) emphasise the need for a just transition, green growth policies, and ensuring that decarbonisation doesn't hinder the progress of developing nations. To truly harness the potential of CCUS, a robust legal and regulatory framework is essential, addressing challenges and facilitating its full-scale deployment.

2.7 Using MCFC for Carbon Capture

MCFCs, operate by using carbonate ions as the charge carriers on the cathode side. They function at temperatures ranging from 550°C to 650°C. This temperature range ensures adequate electrolyte conductivity and chemical reactivity, eliminating the need for expensive noble metal catalysts. A unique feature of MCFCs is their dual capability: they can concentrate CO₂ and produce power simultaneously (182).

Sugiura et al. (183) delved into the potential of MCFCs as carbon dioxide concentrators. Their findings highlighted the importance of the ratio between oxygen and carbon dioxide partial

pressures at the cathode in influencing cell performance. Further research by Campanari et al. (2010) (182) explored integrating MCFCs with Natural Gas Combined Cycles (NGCCs). Their results were promising, indicating a potential 80% reduction in CO₂ emissions with minimal impact on electrical efficiency. Interestingly, this substantial CO₂ reduction was achieved with the MCFC contributing only a fifth of the total power generation.

Chiesa et al. (184) expanded on this by examining the potential of combining cryogenic CO₂ separation with MCFC-integrated combined cycles. They proposed a method to recirculate a portion of the recovered CO₂ in the cathode, offering a way to bypass the oxy-fuel combustion separation presented by Campanari et al. (182)

Sanchez et al. (185) further explored MCFCs by comparing three methods of integrating them with internal combustion engines. Their findings were optimistic, indicating significant carbon emission reductions. They also suggested that future cost reductions, combined with incentives for FCs and reduced carbon emissions, could make MCFCs a compelling technology choice. Their economic analysis considered a small-scale MCFC plant paired with a CHP system, achieving a 63% carbon separation at an overall electrical efficiency of 35% (HHV, net). They believed that performance enhancements could further boost the economic viability of the MCFC-CO₂ capture concept.

Subsequently, Rexed et al. (186), focused on lab-scale MCFC systems using simulated flue gas. Their aim was to demonstrate the feasibility of MCFCs as CO₂ separators for both gas turbine and coal-fired power plants. Milewski et al. (187) and Manzolini et al. (188) both found that MCFCs could significantly reduce CO₂ emissions from power plants. Mamaghani et al. (189) conducted a comprehensive analysis of a hybrid MCFC-Gas Turbine (GT) system, aiming for system optimisation. Lastly, Campanari et al. (190) provided a detailed techno-

economic assessment of using MCFC technology for CO₂ capture from NGCC power plants, examining its implications on electricity and CO₂ capture costs.

2.7.1 Integrating MCFC with cryogenic technology for CO₂ capture

The cryogenic approach involves cooling the anode stream to near the CO₂'s triple point, resulting in the condensation and gravitational separation of most CO₂. This method achieves a CO₂ separation efficiency of 89.3%, producing a CO₂ stream with a purity of 98.8% (mol/mol). This configuration yields a net efficiency of 58.9% (HHV) with a LCOE of €84.66/MWh negating approximately €120.4 per tonne of CO₂ (190).

2.7.2 Integrating MCFC with Oxy-combustion technology for CO₂ capture

Campanari et al. (190) proposed an alternative where residual fuel components are combusted in a boiler using pure oxygen from an ASU. This method results in combustion products primarily consisting of H₂O and CO₂. After water condensation, the dry CO₂ fraction with incondensable species is below 4%. This configuration offers a net efficiency of 57.5% (HHV) and an LCOE of €81.53/MWh at a cost of €107.7 per tonne of CO₂ avoided.

2.7.3 Integrating MCFC with other configurations for CO₂ capture

Duan et al. (191) presented configurations integrating MCFC with both cryogenic separation and afterburners. Another configuration incorporated the Oxygen Ion Transfer Membrane (ITM). These configurations showed that the system's net efficiency could reach up to 63.4% (LHV) with CO₂ capture rates of 85%. The efficiencies were higher than those achieved using cryogenic separation alone.

Greppi et al. (192) introduced an innovative configuration integrating a NGCC-MCFC with Gas Separation Membranes (GSMs) for CO₂ capture. This system achieved an energy conversion efficiency of 52.5% (HHV), although the GSM CO₂ capture system's efficiency

was only 58.1%. The Cost of Electricity (COE) for this configuration ranged between €70.0 and €72.3/MWh.

2.7.4 Integrating MCFC with IGCC

Samanta and Ghosh (193) explored repowering an existing 250 MWe Indian coal-fired thermal power plant by placing an MCFC unit downstream of the existing boiler. This modification increased the plant's net output and efficiency by about 27% and 1.1 percentage points, respectively, capturing 67% of its CO₂ emissions. The COE of the repowered plant was 82\$/MWh, which is 46% higher than the existing plant, with a CO₂ avoidance cost of 43.96\$/tonCO₂. Two studies by Duan et al. (194,195) further scaled up this design, achieving a higher efficiency of 47.3% (HHV, net) but at a higher COE of \$103.85/MWh.

2.8 Identifying Knowledge Gaps

Despite significant advancements in PTG technologies and carbon capture methods, several gaps remain in the current body of knowledge:

- **Integration of Diverse Technologies:**

While individual components such as Solid Oxide Electrolysers (SOEs), Molten Carbonate Fuel Cells (MCFCs), and methanation units have been extensively studied, their integrated operation within a single system remains underexplored. The interactions between these technologies, particularly in terms of thermal management and system efficiency, require further investigation to optimise overall performance.

- **Economic Viability and Scalability:**

Existing studies often focus on the technical feasibility of PTG systems without a comprehensive assessment of their economic viability. There is a need for detailed techno-economic analyses that consider capital and operational expenditures, levelised

cost of energy (LCOE), and payback periods to ensure these technologies can be scaled up for commercial applications.

- **CO₂ Separation and Utilisation:**

Although CO₂ capture techniques have been developed, there is limited research on the efficient integration of these methods with renewable energy sources and fuel cells. Additionally, the utilisation of captured CO₂ in processes such as methanation to produce synthetic fuels needs further optimisation to maximise conversion efficiencies and reduce energy consumption.

Addressing These Gaps

This thesis aims to address these knowledge gaps by:

- Developing and validating an integrated PTG system combining SOEs, MCFCs, SOFCs, and a methanation unit.
- Conducting a comprehensive techno-economic analysis to evaluate the system's economic viability.
- Optimising the process for CO₂ separation and utilisation within the PTG framework.

CHAPTER 3: METHODOLOGY

3.1 Overview of Research Methodology

This chapter outlines the methodological framework employed in this study, which integrates high-temperature electrolyser and fuel cell technologies within a PTG system. The study utilised Aspen Plus™, a powerful process simulation software, to model and simulate the various components of the system. This approach allowed for an in-depth analysis of chemical processes, electrochemical reactions, and the thermodynamics governing the PTG technology.

The core objective of the study was to optimise the efficiency of the system and determine its economic viability by incorporating SOEs, MCFCs, and SOFCs. Aspen Plus was instrumental in simulating the complex unit operations, such as water electrolysis, and carbon capture, along with the heat and mass balance calculations necessary for the PTG system.

In addition to process simulation, a techno-economic analysis was conducted to assess the financial feasibility of the integrated system, focusing on key metrics such as the levelised cost of energy and payback periods. Sensitivity analysis and optimisation techniques were also employed to improve system performance by adjusting various operational parameters, including temperature, pressure, and fuel utilisation rates.

3.2 Modelling and Simulation of fuel cells and related technologies in Aspen Plus

This thesis engages with the modelling and simulation of SOE for steam electrolysis, SOE for steam and CO₂ co-electrolysis, SOFC, MCFC, and methanation unit. Both SOFC and MCFC are high-temperature fuel cells that directly convert chemical energy of variety of fuels into electrical energy. In MCFC, a molten carbonate electrolyte facilitates the transportation of carbonate ions from the cathode to the anode, while oxygen and carbon dioxide react at the cathode to form these carbonate ions. On the other hand, in SOFC, an oxygen ion-conducting ceramic material serves as the electrolyte. Here, the reduction of oxygen takes place at the

cathode to form oxygen ions, which are then transported through the electrolyte to the anode where they oxidise the fuel (196).

The thermodynamic package selected for the simulation of fuel cells and electrolyzers in this study is the "Peng-Robinson method". This method is particularly suitable for hydrogen fuel cell simulations involving key species such as hydrogen, oxygen, and water. Additionally, for fuel cells that use hydrocarbons, it accommodates extra components including carbon dioxide, carbon monoxide, and the hydrocarbon fuels themselves. The choice of the "Peng-Robinson method" is motivated by several factors which include: its suitability for non-polar compounds, its applicability across a wide range of pressures and temperatures, its ability to accurately predict phase behaviour, and its precision in defining pressure-volume-temperature (P-V-T) relationships.

However, Aspen Plus is traditionally employed for simulating processes involving chemical reactions, phase equilibria, and physical transformations, but it lacks built-in capabilities to model electrochemical reactions. This shortcoming necessitates some workaround when simulating processes such as fuel cells and electrolyzers, which fundamentally rely on electrochemical reactions.

To overcome this limitation, the study leverages spreadsheet software (i.e., Excel) to implement the mathematical models associated with the electrochemical reactions, including cell potential, parameters, variables, and energy requirements involved in fuel cells and electrolyzers. The generated data is then communicated to the models in Aspen Plus as updated component properties, allowing the overall system to be modelled and optimised within the Aspen Plus environment.

The detailed modelling and simulation methods for each subsystem unit i.e., steam electrolysis, steam and CO₂ co-electrolysis, SOFC, MCFC, and methanation which include the operating

principles, thermodynamic/electrochemical model details, mass/energy balances, model assumptions and equations, electrochemical processes, reaction pathways, co-electrolysis modelling, and optimisations, are presented in their respective chapters.

3.3 The Simulation platforms data-exchange

Throughout this thesis, and as it has been established earlier, the fuel cell and electrolysis processes involve a wide variety of chemical reactions and transport mechanisms. For instance, the primary electrochemical reaction of splitting water molecules into hydrogen and oxygen occurs at the surface of the electrodes, which requires a catalyst surface site for activation. While a comprehensive and practical model should encompass many of these elements, the final model should also provide optimal computational performance and ease-of-use for the user. A user-friendly design is always a key objective in the development of simulation software. In this research, the aim was to achieve a balance between detailed-modelling and ease of integration with other processes by utilising in-house spreadsheet tools and process flowsheet software.

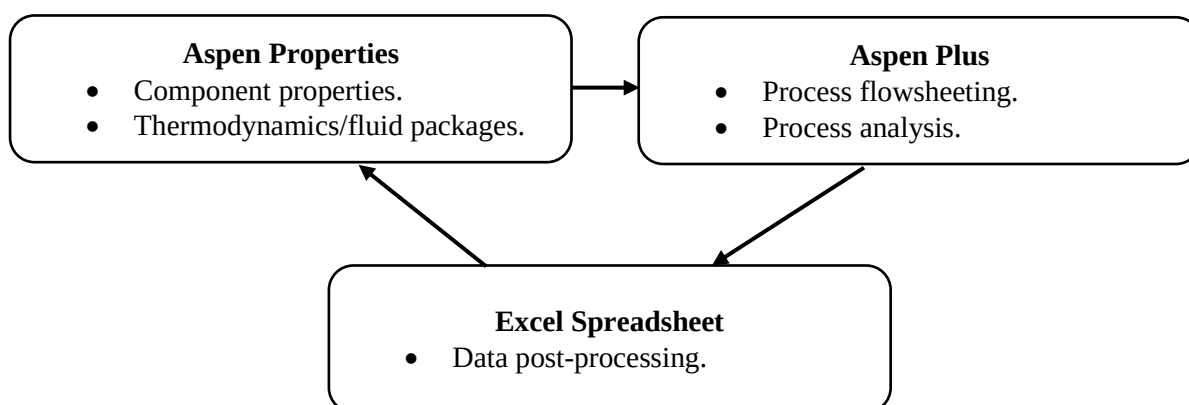


Figure 3.1: The simulation platforms interlined for data exchange.

Figure 3.1 illustrates the interconnectivity of the simulation tools employed in this study, where the emphasis was placed on both the efficiency and ease of conducting calculations without compromising the accuracy of the modelling. The spreadsheet software was utilised to

encode the various electrochemical reactions, mathematical models for cell potential, parameters, variables, and energy requirements or generations involved in the electrolyzers and fuel cells, and the generated data was communicated to the models in Aspen Plus as updated component properties. This iterative process was repeated until results were converged within a reasonable error tolerance. This approach offers flexibility and convenience in adjusting parameter values and configurations, allowing for a detailed examination of the electrochemical and thermal dynamics within an electrolyzer and fuel cell in the Aspen Plus environment. Additionally, this study allowed for the individual estimation of voltage losses and internal temperatures for the anode, cathode, and electrolyte sections, as the simulation relied solely on the inbuilt reactor modules of the software.

3.4 Limitations and Assumptions

The assumptions employed in this study for fuel cells and electrolyzer modelling serve as a simplification of real-world processes to make them computationally feasible. However, these assumptions also impose certain limitations on the simulation process.

The non-dimensional nature of the models limits the impact of scale and size factors on the process. Ignoring pressure drops across unit operation blocks simplifies the simulation but might neglect potential impacts of pressure variations on system performance. The assumption that all operations occur at steady state and are isothermal is convenient for simplification but fails to consider dynamic and thermal gradient effects that might be critical in certain applications. Furthermore, assuming that all fluids obey the ideal gas law might overlook non-ideal behaviour at high pressures or low temperatures. The absence of ion movement simulation in Aspen Plus might limit the accuracy of electrochemical reaction representation.

Both models rely on chemical equilibrium, implying perfect mixing and unlimited reaction time. This assumption can overlook the impacts of kinetics and reaction rates, which can

significantly affect the performance in practical applications. Furthermore, these models always assume the occurrence of water gas shift reaction and steam reforming, neglecting any potential impacts of other chemical reactions or reaction pathways in the fuel cell anode.

3.5 Validation of the Models

The validation process involved a comparison of the simulation results with experimental or literature data. The key metrics used for comparison included I-V curve, j-V curve, energy efficiency, reactant conversion rates, and product distribution.

The models were rigorously tested under various operating conditions and the results were compared with available experimental and literature data. Despite the aforementioned assumptions and simplifications, the models showed a good match with the reference data, suggesting a high level of accuracy and reliability for the studied range of conditions.

However, some discrepancies were noted in certain conditions, potentially arising from the limitations and assumptions inherent in the models. For instance, the models' inability to simulate pressure drop effects and ion movements, or their reliance on ideal gas law and chemical equilibrium, leads to deviations when compared with real-world or more detailed simulations data under extreme conditions such as low or high current density, pressure, among others.

3.6 Methodology for Sensitivity Analysis

Sensitivity analysis serves as a fundamental instrument in comprehending the influence of various parameters on the functionality of fuel cells and electrolyzers. It furnishes us with profound insights into the mechanism of how infinitesimal variations in input determinants can precipitate a substantial sway on the system's output or overall performance.

The methodology employed in this study involved the following steps:

1. **Identification of Key Parameters:** The initial phase in executing the sensitivity analysis involved discerning the essential parameters that could potentially impact the performance of the fuel cells and electrolyzers. This cohort of critical parameters encompassed operational variables such as the composition of the fuel, flow rates, operating temperature, and pressure.
2. **Defining the Range of Variations:** After identifying key parameters, the next step was defining the range of variations for these parameters. This involved setting minimum and maximum values for each parameter, within which the system's response was analysed.
3. **Data Analysis:** The simulation results were then analysed to understand the impact of each parameter on system performance. These were done by examining trends, correlations, or using statistical techniques to quantify the sensitivity of the system's performance to each parameter.
4. **Interpretation of Results:** The final step was the interpretation of results. This involved drawing conclusions about which parameters had the most significant effect on the performance of the fuel cells and electrolyzers, which can then guided optimisation efforts or suggested areas for further investigation.

Via the medium of this sensitivity analysis, the magnitude of influence each parameter wields over the comprehensive system performance were assessed.

3.7 Exergy

Exergy analysis is a tool to assess the efficiency of energy systems, as it quantifies the maximum useful work that can be extracted from a system relative to a reference environment at equilibrium. This thesis incorporates exergy efficiencies calculations to evaluate the performance of the integrated PTG system, including key subsystems like the SOEs, MCFCs,

and SOFCs. By integrating exergy into the thermodynamic analysis, the study aims to identify the irreversibilities within each unit and optimise the system for higher efficiency.

The reference environment used for this analysis is defined as air at 25°C and 1 bar, with the composition of air provided in the standard atmosphere model (including nitrogen, oxygen, water vapour, carbon dioxide, and argon) (197). For chemical exergy, the reference substances in the atmosphere are assumed to be in equilibrium, and all other compounds are considered to have exergy values greater than zero.

3.7.1 Exergy Balance Equations

The exergy balance for an open system (control volume) is expressed as shown in Equation (3.1):

$$\Delta Ex = \Delta Ex_{thermo-mechanical} + \Delta Ex_{chemical} - Exergy\ losses \quad (3.1)$$

Where $\Delta Ex_{thermo-mechanical}$ refers to exergy related to temperature and pressure differences, and $\Delta Ex_{chemical}$ accounts for exergy changes due to differences in composition between the system and the reference environment.

For each subsystem, the exergy inflow and outflow were calculated using the Equation (3.2) for the exergy of a material stream:

$$\psi = (h - h_0) - T_0(s - s_0) + \sum_i \mu_i(T_0, p_0) \cdot x_i \quad (3.2)$$

where h is the specific enthalpy, s is the specific entropy, and μ_i represents the chemical potential of species i at the reference temperature T_0 and pressure p_0 . The chemical exergy of each species is determined based on its concentration and chemical potential relative to the reference environment.

3.7.2 Exergy Calculation for Fuel Cells and Electrolysers

- **MCFC and SOFC:** The exergy of the fuel (e.g., methane, hydrogen) and oxidant (oxygen) entering the fuel cells is calculated, along with the exergy of the products (water, CO₂) and heat. The difference represents the exergy destruction, indicating inefficiencies in the fuel-to-electricity conversion process.
- **SOE:** In the case of electrolysis, the exergy input includes both electrical energy and thermal energy. The exergy of the produced hydrogen or syngas is compared to the exergy of the feedwater and CO₂, with exergy destruction representing inefficiencies in the electrolysis process.

3.8 Economic Analysis

This section focuses on the economic evaluation of the integrated fuel cell and electrolyser system designed for PTG applications. The objective of the economic analysis is to assess the financial viability of the system by calculating key economic indicators such as capital cost, operational cost, and the levelised cost of energy (LCOE).

The methodology adopted for the economic analysis in this study is based on the approach recommended by the National Energy Technology Laboratory (NETL) (198), which has been widely used for evaluating advanced energy systems (199,200). **Table 3.1** presents the model employed in the study.

Table 3.1: Economic analysis models employed in the study

Component cost	Model	Equation No	Ref
SOFC	$(2.96T_{cell} - 1907)A_{SOFC}$	(3.3)	(199)
SOFC auxiliary	$\frac{C_{SOFC}}{10}$	(3.4)	(199)
Post combustion	$\frac{(m_{oxidant})46.08}{1 - (\frac{P_{out}}{P_{in}} + 0.005)} [1 + \exp(0.018 \times T_{out} - 26.4)]$	(3.5)	(199)

Heat exchanger (HX)	$C_{HX,i} = 409(Area_{HX,i}^{0.85} + 20.78)$	(3.6)	(201)
Air and fuel preheater	$C_{preheater} = 2290 \times (Area_{HX,preheater})^{0.6}$	(3.7)	(199)
Total equipment cost of SOFC plant	$C_{Equipment,SOFC\ plant} = (\sum Cost_{component})_{SOFC\ plant}$	(3.8)	(199)
Total engineering, procurement and construction	$C_{EPCC,SOFC\ plant} = C_{Equipment} \times (1 + f_{EPCC})$	(3.9)	(202)
Total plant cost of the SOFC plant	$C_{TPC,SOFC\ plant} = C_{EPCC,SOFC\ plant} \times (1 + f_{TPC})$	(3.10)	(202)
The total overnight cost of the SOFC plant	$C_{TOC,SOFC\ plant} = C_{TPC,SOFC\ plant} \times (1 + f_{TOC})$	(3.11)	(202)
Annual capital cost of SOFC plant	$C_{CAP,SOFC\ plant} = C_{TOC,SOFC\ plant} \times CRF_{SOFC\ plant}$	(3.12)	(199)
MCFC	$C_{MCFC\ stack} = 1500 \times W_{MCFC}$	(3.13)	(199)
Total equipment cost of MCFC plant	$C_{Equipment,MCFC\ plant} = (\sum Cost_{component})_{MCFC\ plant}$	(3.14)	(199)
Total direct plant cost of MCFC plant (TDPC)	$C_{TDPC,MCFC\ plant} = C_{Equipment,MCFC\ plant} \times (1 + f_{INST})$	(3.15)	(203)
Total engineering, procurement and construction cost of MCFC	$C_{EPCC,MCFC\ plant} = C_{TDPC,MCFC\ plant} \times (1 + f_{EPCC})$	(3.16)	(203)
The total overnight cost of the MCFC plant	$C_{TOC,MCFC\ plant} = C_{EPC,MCFC\ plant} \times (1 + f_{OOC})$	(3.17)	(203)
Annual capital cost of MCFC plant	$C_{CAP,MCFC\ plant} = C_{TOC,MCFC\ plant} \times CRF_{MCFC\ plant}$	(3.18)	(199)

MCFC	$C_{MCFC\ stack} = 1500 \times W_{MCFC}$	(3.19)	(199)
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Where A_{SOFC} is the total area of the SOFC module, C_{SOFC} is the capital cost of the SOFC, and T_{cell} is the cell temperature. m , p , and T represent the mass flow rate, pressure, and temperature of the oxidant, respectively. $Area_{HX}$ is the area of the corresponding heat exchanger. f_{EPCC} is the correction factor corresponding to engineering, procurement, and construction, and is taken as 9% for SOFC. f_{TPC} is the correction factor corresponding to process contingencies and project contingencies, taken as 52.5% for SOFC. 'W' is the DC power output from the MCFC stack. f_{TOC} is the correction factor for preproduction costs, inventory capital, owner's costs, and others, taken as 20.2%. f_{INST} is the correction factor corresponding to equipment installation and is taken as 80% of the equipment cost for MCFC and CO₂ removal equipment, and 68% for power plant equipment. f_{EPCC} is also used as the correction factor for yard preparation, service facilities, buildings, and engineering, taken as 14% of the TDPC for MCFC. Finally, f_{OOC} is the correction factor corresponding to planning, designing, and commissioning of the plant, taken as 15% of the EPCC for MCFC.

CHAPTER 4: MODELLING AND SIMULATION OF SOLID OXIDE ELECTROLYSER FOR HYDROGEN GENERATION

4.1 Introduction

At present, fossil fuels are extensively utilised not only for energy production but also as raw materials in several chemical synthesis processes. As the world's energy demand continues to grow, the reliance on fossil fuels has led to the emission of large amounts of greenhouse gases and pollutants (like particulates, sulphur oxides, and nitrogen oxides) which contribute to global warming and pose public health risks (1). Asia, particularly China, has surpassed the US and Europe as the main contributor to emissions (2). Meeting the challenge of reducing CO₂ emissions will require not only increasing the use of zero or negative emission energy sources, but also decarbonising the global conventional energy systems. The target is to reach thermoneutrality by 2050, which means that human activities must emit the same amount of greenhouse gases (GHGs) as can be absorbed through GHG reduction measure (3).

While carbon capture technologies for fossil fuel combustion are still being developed and are currently costly (4–6), achieving this goal will require significant effort and investment.

Consequently, clean energy production from renewable sources like biomass, wind, and solar has gained significant attention in recent times due to concerns about known environmental impacts and the finite nature of fossil fuels. Technologies for electricity generation, such as PV cells and wind turbines, have been widely available, although the output of these technologies is often intermittently available (8) and remains an obstacle to the global deployment. As a result, researchers and policymakers continue to explore methods to enhance the reliability and productivity of renewable energy.

Hydrogen is considered a potential green energy conduit, owing to its high energy density and minimal environmental impact (204,205). As such, it has garnered significant attention from

private and public authorities as it has the potential to meet our energy supply needs and address climate change concerns (206). While hydrogen can be produced from either fossil fuels or through renewable energy technologies, a large fraction (>96%) of the hydrogen currently in use globally is still produced from fossil fuels through various technologies such as gasification, autothermal reforming, partial oxidation, and steam reforming (207), which eventually results in significant carbon emissions.

Water or steam electrolysis is a sustainable and efficient method for producing hydrogen (208). It is considered eco-friendly and has been increasingly adopted as a means of hydrogen production (209). Low-temperature electrolysis technologies, such as Alkaline Electrolysis Cell (AECs) and Proton Exchange Membrane Electrolysis Cell (PEMECs), have low energy conversion efficiency and high production costs due to their reliance on noble metal-based electrocatalysts and high electricity consumption (210). On the other hand, high-temperature electrolysis technologies like SOEs are more efficient and have the potential to utilise medium and high temperature heat sources in the range of 526 °C to 1000 °C (211,212). However, more research is needed to improve their performance from both economic and technical perspectives (213).

Using a mechanistic simulations and models that has been validated against experimental data can be useful in understanding the complex reactions and transport phenomena occurring in a SOE, as it can be challenging to get this information through experiments alone.

Udagawa et al. (214) reported the performance of a cathode-supported IT-SOE 1D model at steady state under different temperatures and current densities. They found that decreasing the current density and increasing the cell temperature reduced the irreversible losses and cell potential in an electrode-supported cell operated on 90% steam concentration at the cathode inlet and 100% O₂ at the anode inlet. It was noted that activation overpotentials predominantly

contributed to these irreversible losses. At a steam temperature of 750 °C and a current density of 700 mAcm⁻², the cell potential was 1300 mV, which is equivalent to 3.1 kW hNm⁻³H₂. Yohei et al. (215) developed a quasi-one-dimensional simulation model of a steam SOE to study the relationship between total overvoltage and the total area-specific resistance. They found that at a temperature of 800°C and a total overvoltage of 1300 mV, a drop in the total area-specific resistance to 150 mΩcm² resulted in a current density of above 1750 mAcm⁻². There are many other models available in literature (216–219) to study the performance of SOE in steam electrolysis. Due to the complexity of currently published simulation models, particularly when integrating them with other process or simulation models to explore various improvement processes to address energy consumption and material degradation issues in the use of SOE for hydrogen production, there exists a demand for the development of a user-intuitive simulation model for SOE. One strategy to accomplish this involves the use of a reputable process modelling tool for conceptual design (i.e., Aspen Plus), to facilitate a more streamlined and intuitive approach to modelling SOE systems.

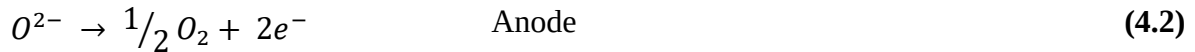
While SOE unit performance improvement is of key importance in improving its efficiency and reducing its operating cost, there are considerable prospects to enhance the SOE process measures when it is embedded in a Balance-of-Plant (BoP) boosting the energy integration and process optimisation potentials. Integration of SOE with other systems may partially compensate its energy and water demands. To explore these opportunities the system level models are of crucial importance. A numerically fast, thermodynamically reliable, and cost-effective SOE simulator is key in proposing, designing, and optimising potential systems.

The goal of this study is to build an accessible Aspen Plus-based model of an SOE. that can easily be integrated into other processes, taking advantage of simulator's comprehensive

thermodynamic and physical property database. Furthermore, it aims to optimise the SOE's operational parameters for maximal hydrogen generation with minimal energy demand.

4.2 Thermodynamics

Equation (4.3) represent the overall cell reaction of water splitting that occurs in a steam SOE.



The entropy and enthalpy change of the water splitting reaction is given as Equation (4.4) and (4.5).

$$\Delta H_{water_splitting}^0 = \Delta H_{H_2}^0 + 0.5\Delta H_{O_2}^0 - \Delta H_{H_2O}^0 \quad (4.4)$$

$$\Delta S_{water_splitting}^0 = \Delta S_{H_2}^0 + 0.5\Delta S_{O_2}^0 - \Delta S_{H_2O}^0 \quad (4.5)$$

Where $\Delta H_{H_2}^0$ is the standard heat of formation of $H_{2(g)}$, $\Delta H_{O_2}^0$ is the standard heat of formation of $O_{2(g)}$, $\Delta H_{H_2O}^0$ is the standard heat of formation of H_2O , $\Delta S_{H_2}^0$ is the standard entropy of $H_{2(g)}$, $\Delta S_{O_2}^0$ is the standard entropy of $O_{2(g)}$ and $\Delta S_{H_2O}^0$ is the standard entropy of H_2O .

Table 4.1: Standard molar enthalpy and entropy of required substance (220)

Substance	Value
$\Delta H_{H_2}^0$	0 kJmol ⁻¹
$\Delta H_{O_2}^0$	0 kJmol ⁻¹
$\Delta H_{H_2O}^0$	-285.85 kJmol ⁻¹
$\Delta S_{H_2}^0$	130.59 JK ⁻¹ mol ⁻¹
$\Delta S_{O_2}^0$	205.29 JK ⁻¹ mol ⁻¹
$\Delta S_{H_2O}^0$	69.964 JK ⁻¹ mol ⁻¹

Taking values of the standard molar enthalpy and entropy of the required substance from **Table 4.1** and by employing Equation (4.4) and (4.5), the standard reaction change in enthalpy $\Delta H_{water_splitting}^0$ and entropy $\Delta S_{water_splitting}^0$ for Equation (4.3) are 285.85 kJmol⁻¹ and 163.25 JK⁻¹mol⁻¹ respectively for one mole of hydrogen gas to be produced with heat of

evaporation inclusive. Consequently, the Gibbs free energy $\Delta G_{water_splitting}^0$ for the reaction is given as:

$$\Delta G_{water_splitting}^0 = \Delta H_{water_splitting}^0 - T \cdot \Delta S_{water_splitting}^0 \quad (4.6)$$

Where T is the temperature (K). The Equation (4.6) indicates that the Gibbs free energy of water splitting reaction is highly temperature dependent and this trend is observed in **Figure 4.1** at operating pressure of 1 atm.

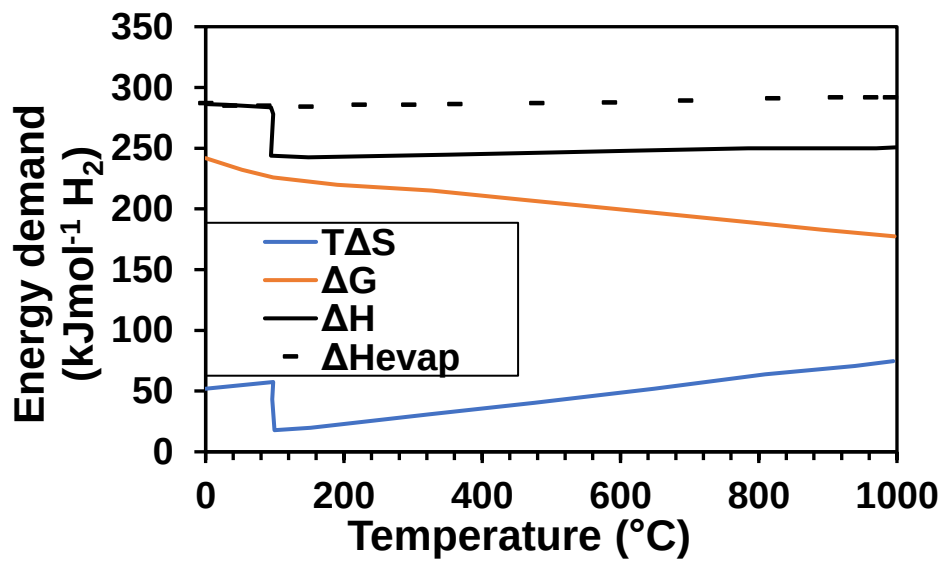


Figure 4.1: Energy demand as a function of temperature, data obtained from (221).

The change in direction of the curve observed in **Figure 4.1** at 100 °C is the heat of evaporation. At a pressure of 1.013 bar, water is in the vapor phase, and as a result, there is no phase change during the reaction. The standard Gibbs free energy of water splitting $\Delta G_{water_splitting}^0$ denotes the electrical energy required for the water splitting reaction. This, however, evident that the operating temperature of the cell greatly influences its performance. Therefore, the electrical energy demand decreases as the operating temperature increases. From Equation (4.6), by calculating $T \cdot \Delta S_{water_splitting}^0$, which represents the heat energy demand for the reaction, the equation gives the difference between $\Delta H_{water_splitting}^0$ and $\Delta G_{water_splitting}^0$ as shown by the blue line graph in **Figure 4.1** (221,222). This confers a notable benefit since an electrolysis cell encounters specific inefficiencies leading to the generation of excess heat at its operational

temperature. By elevating the operating temperature, the capacity to incorporate heat into the electrolysis process amplifies (222). Consequently, high-temperature electrolysis cells like SOEs can approach near-perfect efficiency, reaching close to 100% electrical energy conversion to hydrogen gas (223).

4.3 System Process

The process of a Solid oxide electrolyser starts when an electric current is applied to two electrodes, which are separated by a solid electrolyte as shown in **Figure 4.2**.

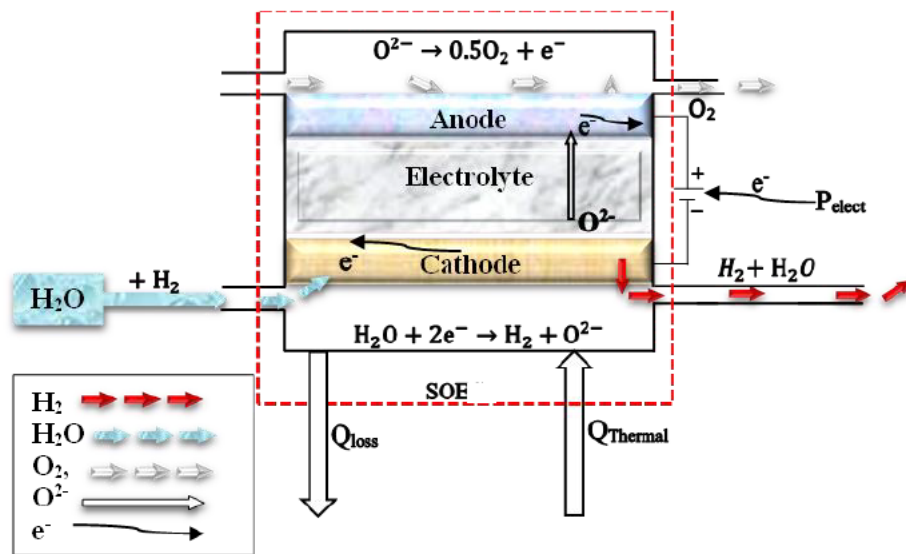


Figure 4.2: Solid oxide electrolyser

The general process of a SOE adopted in the study is summarised as follows:

- Preheating: The cathode and anode sides are preheated (denoted Q_{Thermal}) to the required operating temperatures to ensure efficient and stable operation.
- Electrode reactions: At the cathode, hydrogen ions are generated and reduced to hydrogen gas through a hydrogen-reducing reaction, while at the anode, oxygen ions are produced through an oxygen-evolving reaction as shown in **Figure 4.2** and Equation (4.1) and (4.2).

- **Ionic transport:** The solid oxide electrolyte serves as a pathway for the transport of hydrogen and oxygen ions between the cathode and anode.

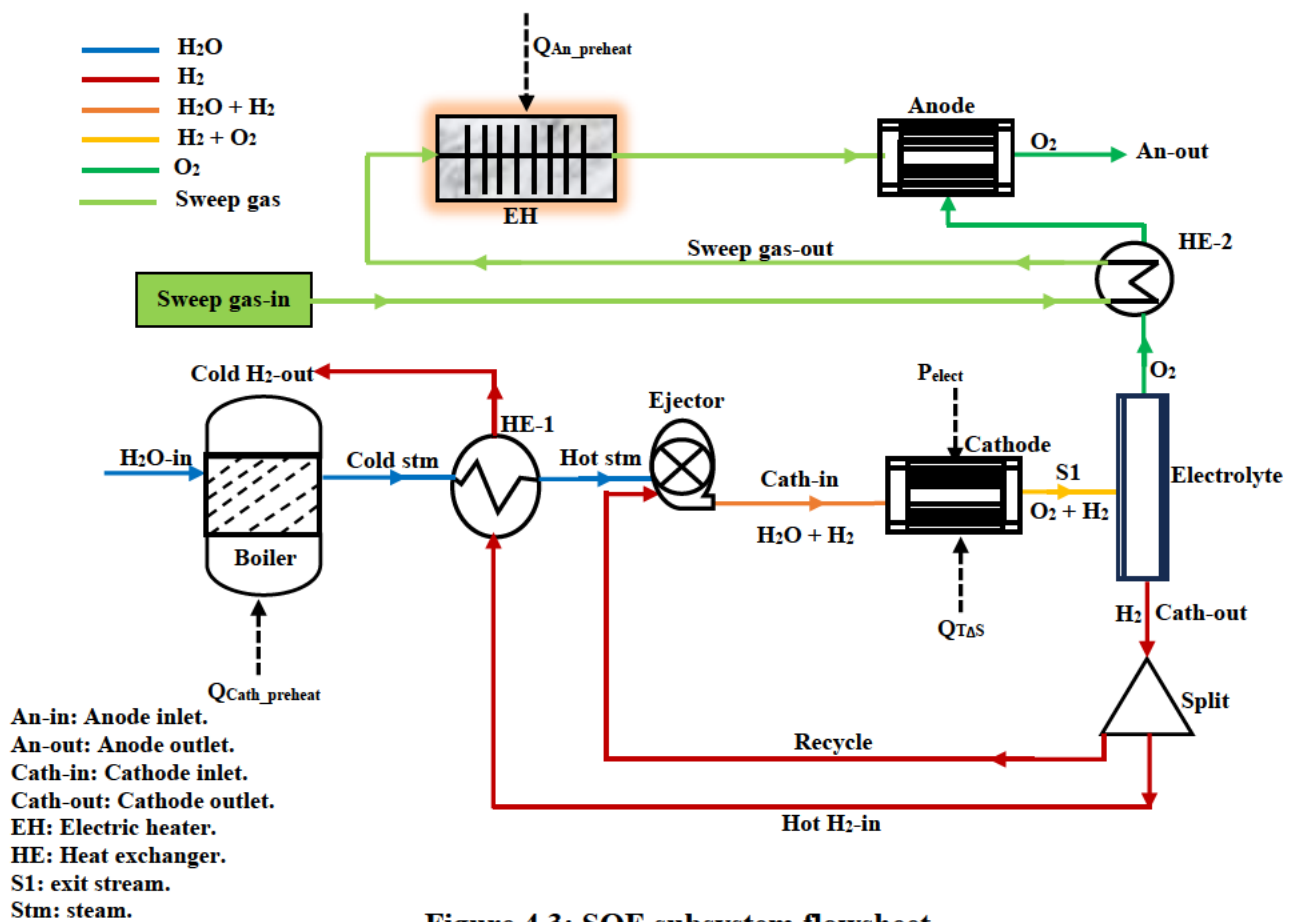


Figure 4.3: SOE subsystem flowsheet

This subsystem shown in **Figure 4.3** consists of SOE main reactor and auxiliary units which exist to support the SOE operation, such as heat exchangers, mixers, etc. The lines' pressure drops are ignored. The hot steam stream (Hot stm) originating from the boiler, having undergone preheating via heat exchanger 'HE-1' utilising the hot exhaust stream from the SOE cathode, serves as the primary feed for the electrolyser. Prior to entering the electrolyser, the hot steam stream is mixed with recycled hydrogen gas exiting the cathode channel (Recycle) to mitigate cathode nickel oxidation (224). The in-built RSTOIC reactor model is utilised to model the cathodic electrochemical reaction of the steam at the temperature of interest. The overall cell reaction as shown in Equation (4.3) is considered in the 'CATHODE' block.

For simulation purposes, the discharge stream (S1) from the cathode is first passed through the separator (Elect) block to separate hydrogen and oxygen. The oxygen is then directed to the anode, simulating the movement of O^{2-} through the electrolyte. The remaining stream (Cath-out), which contains a mixture of hydrogen and steam, is then split at the SPLIT block into 'Recycle' and 'Hot H_2 -in' streams. The ratio of splitting is calculated and adjusted until the desired steam to hydrogen ratio of 9 to 1 is achieved at the EJECTOR block, as per the feed specifications. The sweep gas, denoted as "Sweep gas-in" in the model, is preheated using heat exchanger (HE-2), which utilises the hot exit stream from the cathode through the electrolyte "Elect" block to simulate the transfer of heat between the electrodes in the model. The sweep gas-in serves the purpose of transporting the $O_{2(g)}$ generated at the electrolyte's surface at the anode, as shown in Equation (4.2). Additionally, it serves as a means of transferring heat between the anode and cathode. Therefore, the heater (EH) supplies the remaining heat denoted as ($Q_{An-preheat}$) to the sweep gas to maintain both electrodes at the desired reaction temperature. The sweep gas can be oxygen, steam, or air, while in this case, oxygen is being used.

4.4 The electrical and thermal energy required computation

The computation of cell voltage in the simulation of every electrolytic cell or fuel cell is the most important aspect. The cell potential is determined from both the equilibrium potential and overpotential. The equilibrium potential (E_{eq}) is essentially the voltage difference between the electrode and an electrolyte, which provides insight into the minimum electrical energy required to support the reaction. It is determined by the thermodynamic properties of the materials used in the SOE, such as the electrode materials, electrolyte, and the operating temperature. It can be derived using the Nernst equation, which relates the cell potential to the standard electrode potentials of the half-reactions measured in volts (E^0), the concentrations of the reacting species (P_{H_2O} , P_{H_2} and P_{O_2}) measured as partial pressures of water vapour, hydrogen, and oxygen (kPa) respectively, the operating temperature of the cell (T) measured

in Kelvin, the universal gas constant (R) with a value of $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and Faraday's constant (F) with a value of 96485 C mol^{-1} as shown in Equation (4.7) and (4.8).

$$E_{eq} = E^0 + \frac{RT}{2F} \ln \left[\frac{p_{H_2} p_{O_2}^{0.5}}{p_{H_2O}} \right] + \left(\frac{RT}{2F} \right) \ln \left(\frac{P}{P_0} \right) \quad (4.7)$$

with

$$E^0 = 1.253 - 2.4516 \times 10^{-4} T \quad (4.8)$$

$$p_x = y_x P \quad (4.9)$$

and p denoting partial pressures, whereas P is the absolute pressure and P_0 the pressure at standard conditions. The second part of Equation (4.7) uses the relation between partial and absolute pressure to deconvolute the influence of both parameters.

There are three main electrical energy losses to be considered for voltage calculation which are otherwise known as the overpotentials. These include, the ohmic, the activation and the concentration overpotentials (225).

Ohmic overpotential (E_{ohm}), also known as Ohmic resistance or IR drop, refers to the electrical resistance present in an electrolyte that causes a loss of energy during the electrolysis process. It is the excess potential required to drive the current through the cell and is a consequence of the electrical and ionic resistance of the cell. This energy loss results in a decrease in the overall efficiency of the electrolysis reaction and is typically measured in volts and calculated from Equation (4.10) (226).

$$E_{ohm} = 2.94 \times 10^{-5} (JL) \exp \left(\frac{10300}{T} \right) \quad (4.10)$$

Where J and L indicate the current density (A m^{-2}) and electrolyte layer thickness (m) respectively.

The activation energy overpotential (E_{act}), which is the energy loss due to the activation energy barrier that needs to be overcome for the electrochemical reactions to proceed at the electrode surface. It can be reduced by using a catalyst, or by using a different electrode material that has

a lower activation energy. It can be determined using equations obtained from the Butler-Volmer equation (227) for reaction kinetics and charge transfer rates at the electrode/electrolyte interface, shown in Equation (4.11) and (4.12) (226).

$$E_{act,i} = \frac{RT}{F} \sinh^{-1} = \frac{RT}{F} \ln \left[\frac{J}{2J_{o,i}} + \sqrt{\left(\frac{J}{2J_{o,i}} \right)^2 + 1} \right] \quad (4.11)$$

$$J_{o,i} = k_i \exp \left[-\frac{E_{a,i}}{RT} \right] \quad (4.12)$$

Where, $J_{o,i}$ represent the exchange current density at i (which indicates either the cathode or the anode) (in units of Am^{-2}), k_i represent the frequency factor at the anode and cathode (Am^{-2}), and $E_{a,i}$ is the activation energy of the anode and cathode ($\text{Jmol}^{-1}\text{K}^{-1}$).

Concentration overpotential (E_{conc}), also known as concentration polarisation, refers to the effects of concentration gradients on the kinetics of the electrolysis reaction. In other words, it is the decrease in the electrode potential caused by an increase in the concentration of reactants or products at the electrode surface during an electrochemical reaction. This can occur when the rate of mass transport of reactants or products to or from the electrode surface is slower than the rate of the electrochemical reaction taking place. This also results in a decrease in the overall efficiency of the reaction and can be reduced by increasing the surface area of the electrode or by using a catalyst to increase the rate of the electrochemical reaction. It can be estimated using Equation (4.13) and (4.14) (216,221).

$$E_{conc,cat} = \frac{RT}{2F} \ln \left[\frac{\left(1 + \frac{JRTd_{cat}}{2FD_{H_2O}^{eff}P_{H_2}} \right)}{\left(1 - \frac{JRTd_{cat}}{2FD_{H_2O}^{eff}P_{H_2O}} \right)} \right] \quad (4.13)$$

$$E_{conc,an} = \frac{RT}{2F} \ln \left[\sqrt{1 + RTJd_{an}/4FP_{O_2}D_{O_2}^{eff}} \right] \quad (4.14)$$

Where d_{an} and d_{cat} denotes the thicknesses of the anode and cathode (measured in meters) respectively, $D_{O_2}^{eff}$ and $D_{H_2O}^{eff}$ are the effective diffusion coefficient of oxygen and steam (m^2s^{-1}) respectively.

Given the straightforward approach of Fick's model and its efficacy in elucidating gas transport phenomena, this study employed its modified form, as presented in Equation (4.15) (228), to determine the effective diffusion of O_2 and steam.

$$D_x^{eff} = \frac{1}{\left[\left(\frac{\xi}{\phi} \right) \cdot \left(\frac{1}{D_{v-x}} + \frac{1}{D_{x,k}} \right) \right]} \quad (4.15)$$

Where D_x^{eff} denotes the effective diffusion of x , $D_{x,k}$ represents the Knudsen diffusion of x , D_{v-x} represents the molecular diffusion coefficients of v and x (m^2s^{-1}), and the subscripts v and x denote the colliding species composing the binary gas mixture, with hydrogen and steam at the cathode, and oxygen, nitrogen, or steam at the anode, respectively, which were calculated using Equation (4.16) - (4.18):

$$D_{x,k} = 2.13r \sqrt{\frac{RT}{M_x}} \quad (4.16)$$

$$D_{v-x} = \left[\sqrt{\left(\frac{M_v + M_x}{M_v M_x} \right) 1.7689 \times 10^{-6}} \right] \cdot \left[\frac{T^{1.5}}{(0.25 \cdot \Phi_D \cdot P \cdot (\sigma_v + \sigma_x)^2)} \right] \quad (4.17)$$

$$\Phi_D = 10^{-2} \left[\frac{353}{2(49.11)^{\frac{T}{(\varepsilon_{v-x}/k)}}} + \frac{259}{2.5(4.62)^{\frac{T}{(\varepsilon_{v-x}/k)}}} + \frac{19}{(1.61)^{\frac{T}{(\varepsilon_{v-x}/k)}}} \right] + \left[\left(\left(\frac{T}{\varepsilon_{v-x}/k} \right)^{-0.1561} \right) \cdot 1.6036 \right] \quad (4.18)$$

Where r represents the electrode's mean pore radius (m), Φ_D is the dimensionless diffusion collision integral, M_v & M_x are the molar masses of v and x , respectively ($gmol^{-1}$), σ_v & σ_x are the mean diameter, ξ represents the tortuosity of the electrode, ϕ denotes the porosity of the electrode, and ε_v/k & ε_x/k represent the potential constants of the Lennard-Jones (229) of v , and x (K) respectively.

Therefore, total overpotential losses (E_{T_loss}) becomes:

$$E_{T_loss} = E_{ohm} + E_{act,i} + E_{conc,an} + E_{conc,cath} \quad (4.19)$$

Consequently, as shown in Equation (4.20), the SOE cell voltage (V) becomes the combined result of the estimated equilibrium Nernst voltage (E_{eq}) calculated using Equation (4.7) and the total overpotential losses E_{T_loss} shown in Equation (4.19).

$$V = E_{eq} + E_{T_loss} \quad (4.20)$$

Also, the cell current (I) in ampere was determined from the Equation (4.21) by specifying the required steam utilisation factor.

$$I = n_e F \dot{n}_{H_2O} U_{steam} \quad (4.21)$$

Where, n_e indicates the number of moles of electrons consumed per mole of hydrogen produced, $\dot{n}_{H_2O}$ denotes molar flow rates of steam feed (mols⁻¹) and U_{steam} is the steam utilisation factor.

And the current density (j) is calculated from the cell current (I) and cell area (A) as shown in Equation (4.22)

$$j = \frac{I}{A} \quad (4.22)$$

Consequently, the electrical power demand (P_{elect}) of the solid oxide electrolytic cell, measured in watts (W), is estimated using Equation (4.23).

$$P_{elect} = IV \quad (4.23)$$

The total energy demand (Q_T) for the Solid oxide electrolyser, consists of electrical (P_{elect}) and thermal ($Q_{Thermal}$) energy as shown in **Figure 4.2**.

The SOE operation involves irreversible reactions as current is passed through the electrolyte, resulting in the production of heat known as Ohmic heating (Q_{Gen}) presented by the Equation (4.24).

$$Q_{Gen.} = E_{Ohm} \cdot I \quad (4.24)$$

The Combined heat requirement ($Q_{Thermal}$) for the functioning of the SOE can be determined using Equation (4.25).

$$Q_{Thermal} = (Q_{Cath_preheat} + Q_{T\Delta S} + Q_{An_preheat}) - Q_{Gen} \quad (4.25)$$

where $Q_{Cath_preheat}$ represents the thermal energy required on the cathodic side of the reaction, specifically for steam generation, $Q_{T\Delta S}$ is the thermal energy required for the water splitting reaction, $Q_{An_preheat}$ denotes the thermal energy required on the anodic side of the reaction, primarily for preheating the sweep gas, and Q_{Gen} stands for the internally generated heat energy through ohmic heating.

The cell's overall energy efficiencies (Eff_{SOEC}) were estimated from Equation (4.26).

$$Eff_{SOEC} = \frac{n_{H_2,out} \cdot LHV_{H_2} + Q_{Out}}{P_{Elect} + Q_{Thermal}} \quad (4.26)$$

where $n_{H_2,out}$ denotes H_2 molar flow rate produced (mols^{-1}), LHV is the Lower Heating Value of H_2 (Jmol^{-1}) and Q_{Out} is the heat released by the exiting streams of system.

4.5 Validation of the SOE model

The SOE model was validated using experimental data from Bernadet et al., (2015) (224), who explored the effect of pressure on the j-V curve of SOEs through both experimental and modelling approaches. The cell used in the study consisted of a thick layer of Ni-8YSZ (8 mol% Y_2O_3 - ZrO_2 , 500 μm thick, 35 mm in diameter) as fuel electrode and substrate, a thin layer of 8YSZ (5 μm) as electrolyte, an intermediate layer of Gd-doped CeO_2 (CGO, 2 μm), and a $LaSrCoO_{3-\delta}$ (20 μm) layer as the air electrode.

Table 4.2: Model input parameters for validation

Model input parameters	Value	Unit	Reference
Operating temperature, T	800	°C	(224)
Operating pressure, P	1 to 10	bar	(224)
Exchange current density of the anode ($j_{0,an}$)	2.08×10^4	Am^{-2}	(224)
Exchange current density of the cathode ($j_{0,cat}$)	2.24×10^4	Am^{-2}	(224)
Activation Energy of the cathode ($E_{a,cat}$)	100	kJmol^{-1}	(218)
Activation Energy of the anode ($E_{a,an}$)	120	kJmol^{-1}	(218)
Electrode porosity of anode, (ϕ)	0.43		(224)
Electrode porosity of cathode, (ϕ)	0.46		(224)
Electrode tortuosity of anode (ξ)	4.0		(224)
Electrode tortuosity of cathode (ξ)	7.8		(224)
Average pore radius, r	1.2×10^{-06}	m	(224)

The cell was maintained at a constant temperature of 800°C and pressure of 10 bar, with dry air as the sweep gas at the air electrode and a flow rate of $24 \text{ NmLmin}^{-1}\text{cm}^{-2}$, and a mixture of nitrogen, steam, and hydrogen (mole fractions 0.35, 0.585, 0.065 respectively) at the fuel electrode with a flow rate of $18.56 \text{ NmLmin}^{-1}\text{cm}^{-2}$. **Table 4.2** lists the input parameters for the model, while **Figure 4.4** shows comparison of the model predictions and experimental polarisation curves.

Table 4.3: Comparison between the experimental data (224) and model results.

Current Density (Acm^{-2})	Steam Conversion (%)	Exp (V)	Model (V)	Relative error (%)
-1.424	92.261	1.320	1.322	0.173
-1.379	89.226	1.300	1.301	0.115
-1.333	86.039	1.272	1.279	0.547
-1.297	82.853	1.255	1.251	0.336
-1.239	78.756	1.230	1.226	0.360
-1.135	74.962	1.202	1.197	0.388
-1.065	70.561	1.191	1.172	1.577
-0.975	62.064	1.162	1.149	1.048
-0.855	55.235	1.131	1.120	0.981
-0.764	45.220	1.106	1.114	0.758
-0.667	41.730	1.083	1.108	2.274
-0.554	33.991	1.054	1.100	4.334
-0.439	29.287	1.034	1.091	5.589
-0.329	22.003	1.008	1.082	7.247
-0.230	15.023	0.979	1.069	9.150
-0.155	9.105	0.956	1.051	9.938
-0.080	6.525	0.939	1.024	9.042
-0.023	1.669	0.914	0.913	0.027
0.005	0.152	0.900	0.893	0.783

The relative errors ranged from 0.03% to 9.9% as presented in **Table 4.3**. The maximum relative error was found at a steam conversion of 9.1% and current density of -0.16 Acm^{-2} , and the minimum relative error was observed at a steam conversion of 1.7% and a current density of 0.02 Acm^{-2} . It can be observed that the model accurately describes the open-circuit voltage (OCV) in regions where the concentration overpotential at the cathode is dominant, primarily at higher current densities, as shown in **Figure 4.5**.

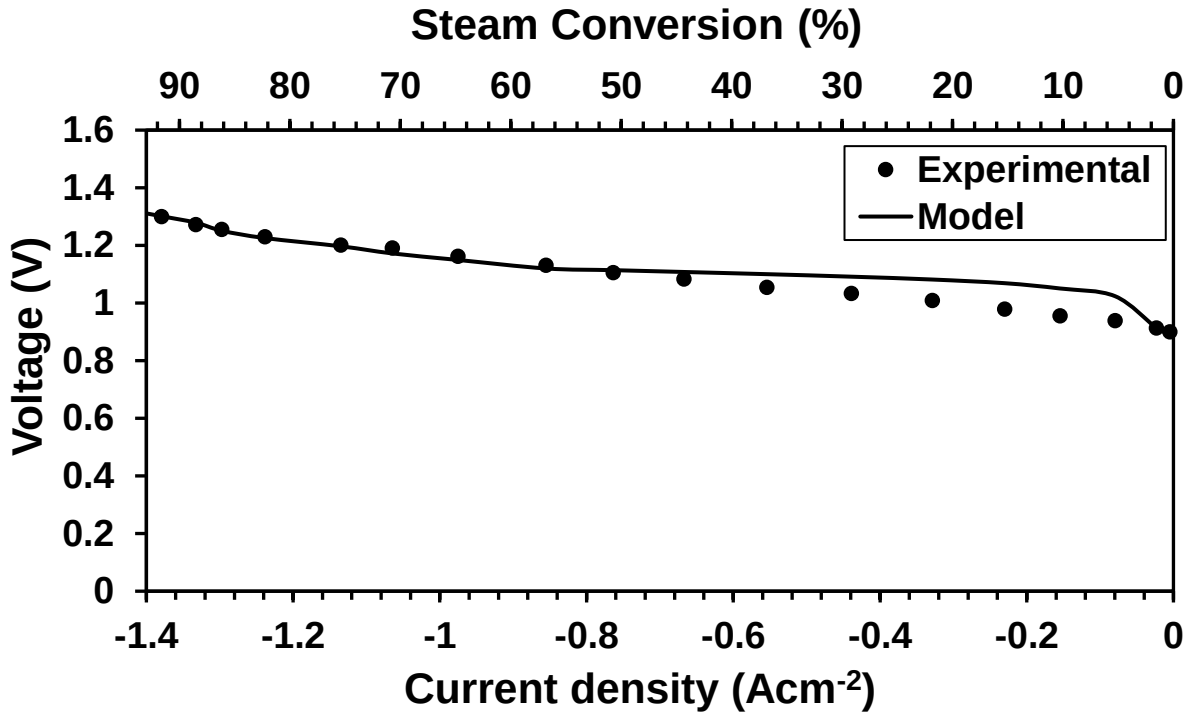


Figure 4.4: Model predictions and experimental polarisation curves (experimental data from (224))

However, the model seems to overestimate the activation energy overpotential in regions of lower current densities for this particular comparison, since the wider literature aligns with our model. A potential rationale for the discrepancies could stem from inconsistencies in values for stream flow rates or inaccuracies in the microstructural properties of the thick cathode support. It's worth noting that the microstructural parameters of the anode do not significantly affect the limiting current density of the cell, given that the gas diffusion through the thin electrode is not a limiting factor. Furthermore, overall, a correlation coefficient of 0.964 was estimated, indicating a reasonable agreement between the model's predictions and the experimental data. Consequently, the model demonstrates good performance when compared to experimental data, providing confidence in its predictive capabilities for SOE performance.

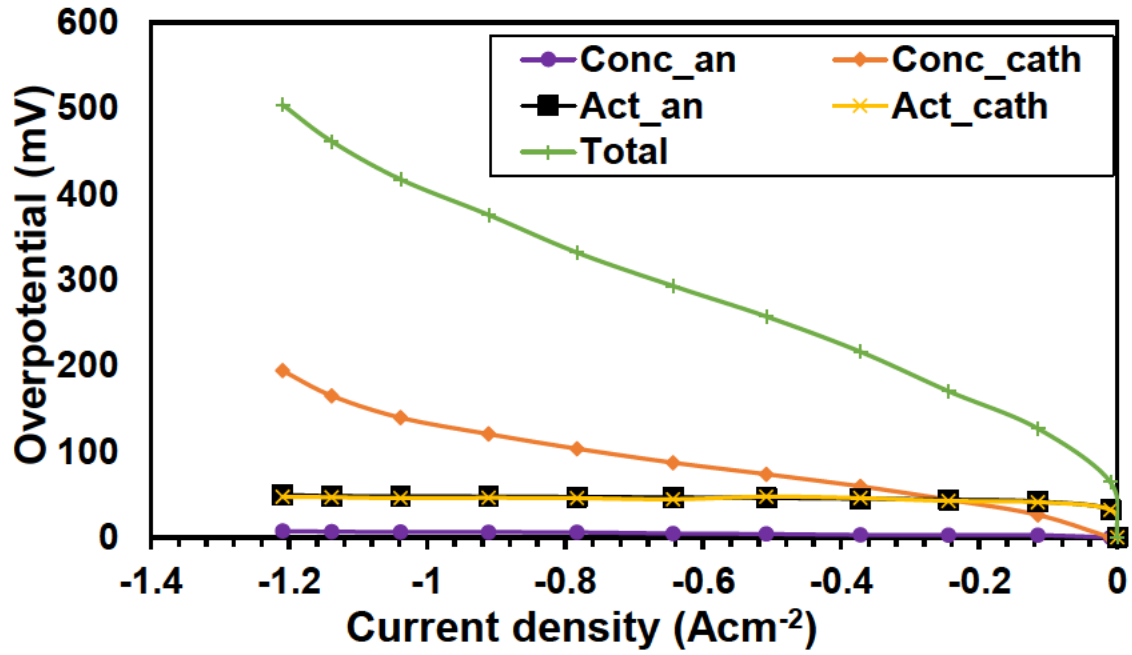


Figure 4.5: Plot of current density vs overpotentials where Conc_an indicates the anode concentration overpotential, Conc_cath indicates the cathode concentration overpotential, Act_an indicates the anode activation energy overpotential, Act_cath indicates the cathode activation energy overpotential and Total is the total overpotential.

4.6 Results and discussions

The validated model was applied to investigate the SOE operation and explore optimisation opportunities. The SOE operating condition optimisation is multi-variable-multi-objective challenge. It requires multifaceted data-driven evaluations of highly nonlinear and interactive mechanisms involved in SOE operation. To this end, the developed platform in this work benefits computation time and accuracy as shown in following sensitivity analyses and optimisation cases.

4.7 Effect of operating parameters

The key barrier to the widespread application of SOEs is their total cost, which is mainly due to their extensive power demand. Optimisation of the operating conditions is central to addressing this problem.

In this section, the model is applied to perform a sensitivity analysis based on dominant operating variables. The outcomes support decision-making in practical optimisation, where

insight from an in-depth sensitivity analysis is essential for manipulating variables and determining their variation boundaries.

4.7.1 Effect of cell operating temperature

As the operating temperature has a significant impact on the Nernst voltage and reaction kinetics, it is necessary to consider the effect of operating temperature on SOEs to optimise their performance. Further studies are also necessary to better understand the underlying mechanisms and develop strategies to mitigate the increase in voltage loss at elevated temperatures.

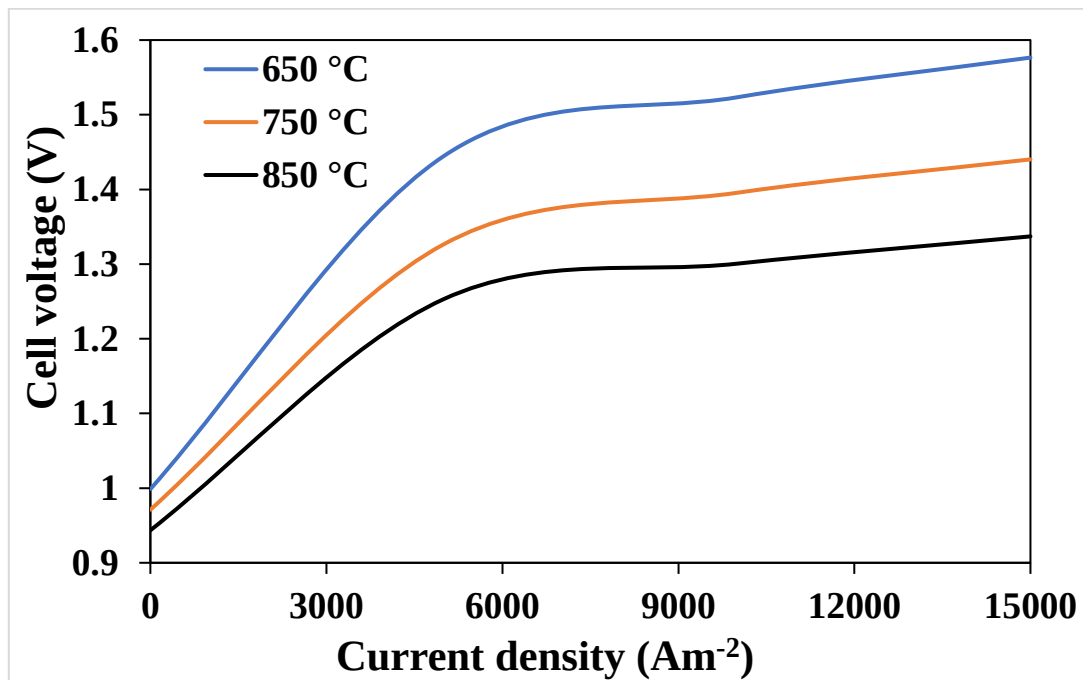


Figure 4.6: Effect of cell temperature on J-V curve at 1 bar, 90% steam concentration and air as anode sweep gas.

A sensitivity parameter study on the J-V curve was conducted, as shown in **Figure 4.6**, for cell operating temperatures in the range of 650 to 850 °C. The cathode was supplied with a steam-hydrogen mixture at a ratio of 9:1, and air was supplied as the sweep gas at the anode. It was observed that increasing the cell operating temperature decreases the open-circuit voltage, resulting in a lower operating voltage. The best performance was observed at a temperature of

850 °C within a range of 0.95–1.34 V, which is consistent with experimental results reported in (230).

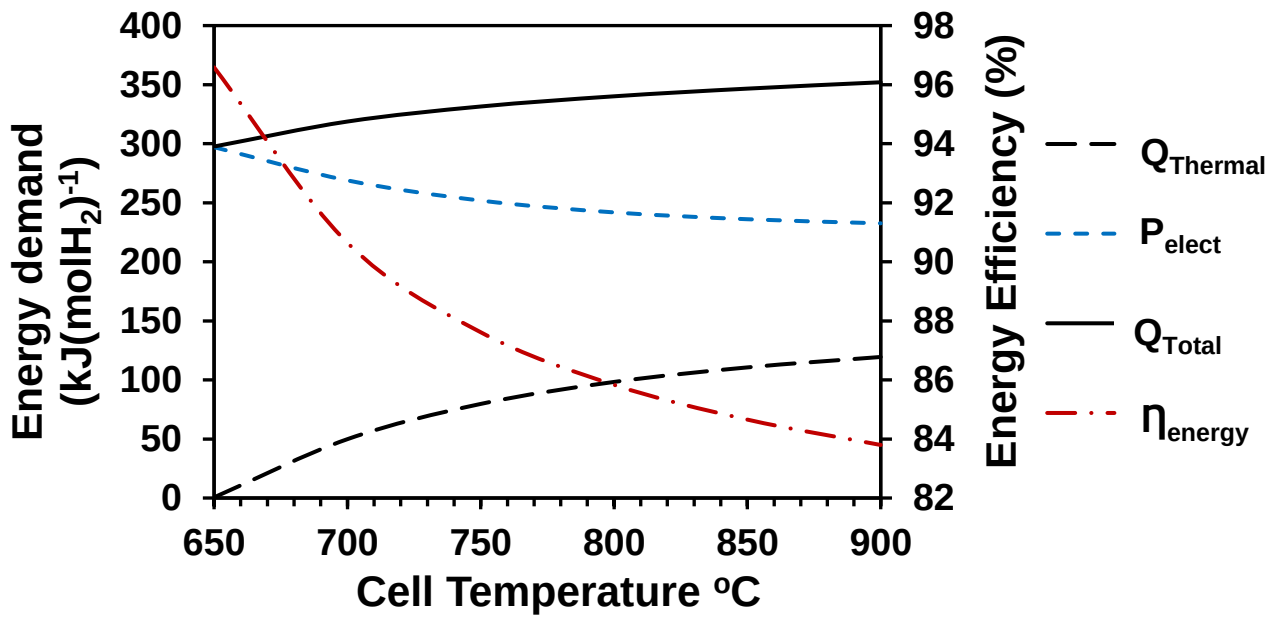


Figure 4.7: Effect of temperature on energy demand. Where Q_{Thermal} is the thermal energy demand, P_{elect} is the electrical energy demand, Q_{T} is the total energy demand and η_{energy} is the energy efficiency of the SOE

The effect of operating temperature is also observed on the total energy demand of the system, as shown in **Figure 4.7**. The figure shows a slight increase of the total energy demand to about 352 kJ(molH₂)⁻¹ as the temperature is increased to 900 °C, while the thermal energy demand also rises to about 120 kJ(molH₂)⁻¹ due to the elevated cell operating temperature. However, the electrical energy demand decreases to about 233 kJ(molH₂)⁻¹, as shown in **Figure 4.7**, which is consistent with the results presented in **Figure 4.6**.

4.7.2 Effect of steam-to-hydrogen feed ratio

The effect of steam-to-hydrogen ratio on the performance of a SOE was investigated in a range from 25% to 90% steam, operating with pure oxygen at the anode and at a temperature of 750 °C.

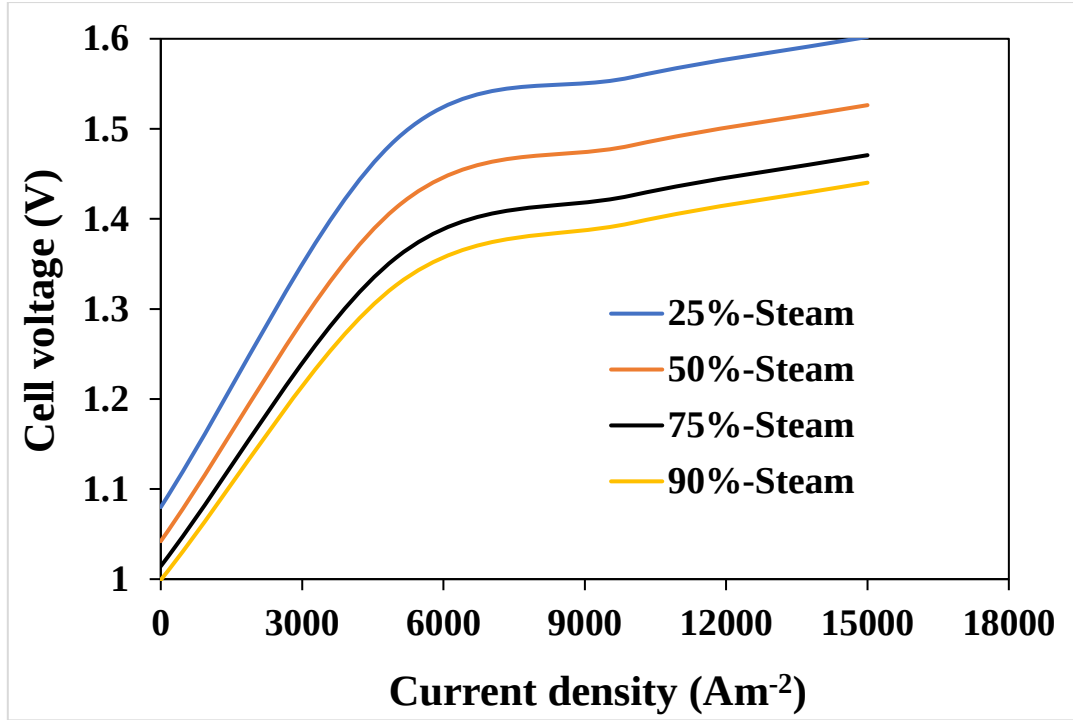


Figure 4.8: Effect of steam-to-hydrogen feed ratio on J-V curve at 750 °C, and pure O₂ as anode sweep gas

Results indicate that a higher steam concentration provides improved performance in the electrolytic cell. The deviation observed at low current levels is attributed to a decrease in the Nernst voltage, as described in Equation (4.7). Increased losses at high current densities result from larger diffusion losses at the anode.

As seen in **Figure 4.8**, improved electrolysis performance is achieved with higher steam concentrations and lower hydrogen levels, consistent with the findings reported by Buttler et al. (221).

4.7.3 Effect of steam utilisation factor

The **Figure 4.9** shows the effect of steam utilisation factor from 60% to 95% on the energy balance of the system at a temperature of 700 °C, current density of 2071 Am⁻² with pure oxygen at the anode, and pressure of 1 bar.

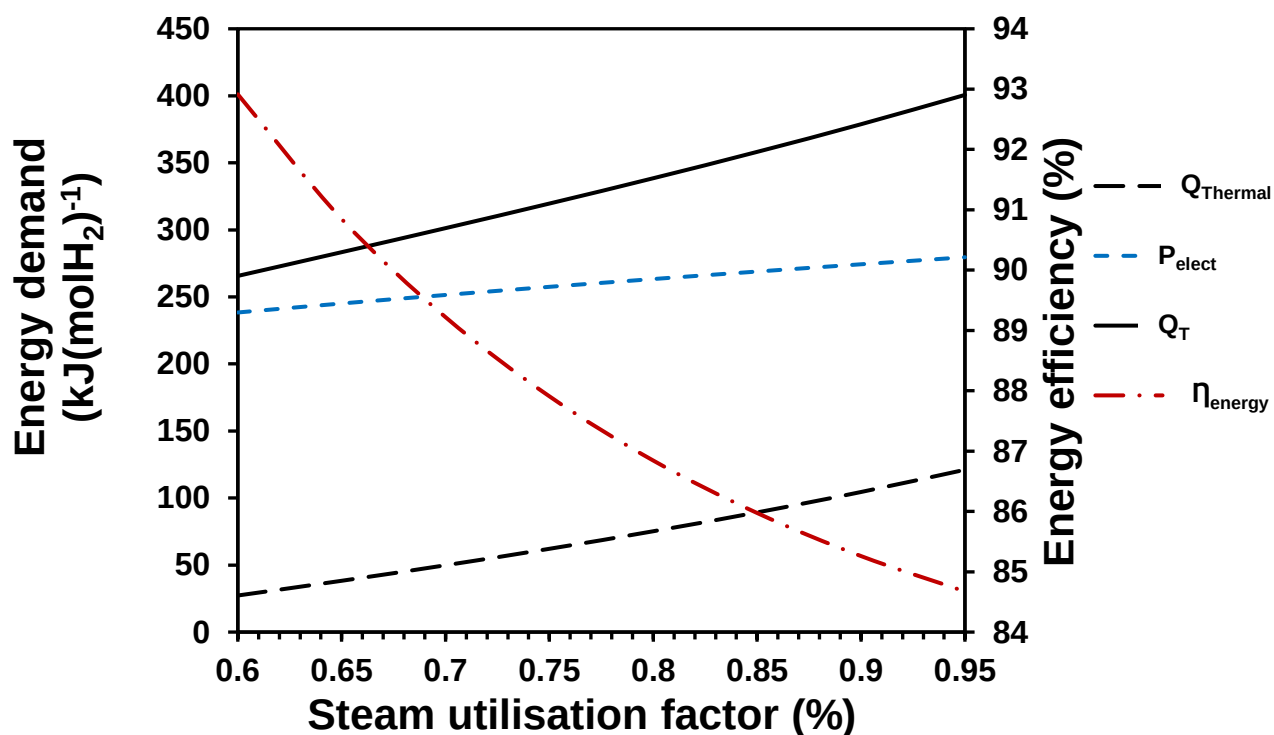


Figure 4.9: Effect of steam utilisation factor

As observed in **Figure 4.9**, the thermal energy demand increased to about $121 \text{ kJ(molH}_2\text{)}^{-1}$ at 95% steam utilisation, meaning that more heat energy was required to maintain the temperature of the system. The electrical energy demand also increased to about $280 \text{ kJ(molH}_2\text{)}^{-1}$, which is likely due to the higher utilisation of steam resulting from an increase in the electrical resistance in the system and thus a higher demand for electrical energy to drive the process. As a result of these two factors, the total energy demand of the system increased to about $400 \text{ kJ(molH}_2\text{)}^{-1}$. The decrease in energy efficiency to around 85% observed at 95% steam utilisation can be attributed to decreased transport of reactants and products to and from the electrodes, and increased polarisation of the electrodes from the higher steam utilisation factor, which also results in increased thermal energy transfer from the steam to the electrodes and electrolyte in the SOE.

Finally, the decrease in energy efficiency of the system to 84.4 % at 95% steam utilisation as shown in **Figure 4.9** indicates that less of the energy input into the system is being converted

into useful output, which is a concern and could impact the overall performance of the system. These results are consistent with previous studies (231–234) that have investigated the impact of steam utilisation factor on energy efficiency in SOEs. These findings highlight the importance of considering the steam utilisation factor when optimising energy efficiency in SOEs.

4.7.4 Effect of pressure

The performance of a SOE is influenced by its operating pressure, as it's a function of the partial pressures as outlined in Equation (4.7). Nevertheless, performing experiments under increased pressure conditions is challenging due to the risk of cracking and leakages (235). A study was conducted to compare the effects of three different pressures at 90% steam concentration at the cathode, sweep-in gas of pure O₂ at the anode, and at a temperature of 750 °C.

As depicted in **Figure 4.10**, the simulation findings suggest that the Nernst voltage experiences an increase with rising pressure when current densities exceed 3000 Am⁻², concurrently resulting in a reduction of diffusion losses. This is most apparent when comparing atmospheric pressure to 10 bar. Albeit the increase in open circuit cell voltage is less than ideal, it is counterbalanced by diminished diffusion losses beyond a specific current density. This observation aligns with the results reported by Bernadet et al. (224). In **Figure 4.10**, the identified points of convergence for the operating pressure at 1 and 10 bar are positioned at 3000 Am⁻². As the reaction kinetics in the electrolyte are limited by chemical equilibrium, increasing the pressure to 20 bar will increase the Nernst voltage. However, this increase in Nernst voltage does not result in a proportionate increase in reaction kinetics, but instead, a gradual increase in the reaction rate. The optimal choice of pressure for optimal performance

will depend on the specific cell and operation parameters, which aligns with the findings of Wendel et al. (236).

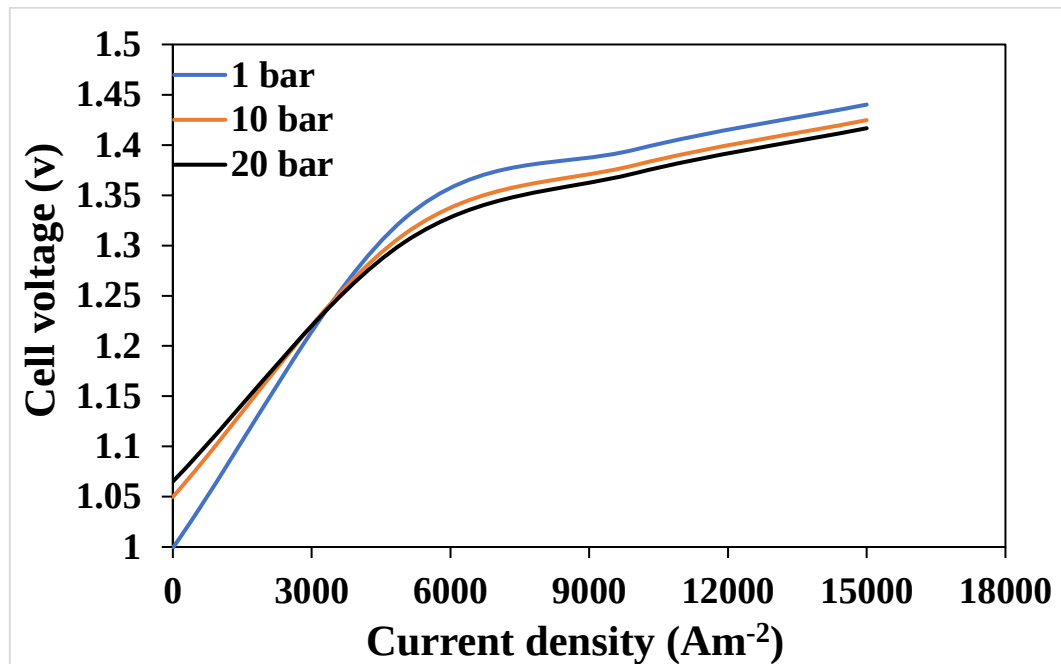


Figure 4.10: Effect of cell operating pressure on J-V curve at cell temperature of 750 °C, pure O₂ as anode sweep gas and 90% steam concentration.

4.7.5 Effect of current density

The results of increasing the current densities in the SOE from 500 Am^{-2} to 2500 Am^{-2} suggest that there is an increase in electrical energy demand to about $277 \text{ kJ}(\text{molH}_2)^{-1}$ at 2500 Am^{-2} as shown in **Figure 4.11**, which is in line with the expected trend of higher current leading to higher electrical energy consumption.

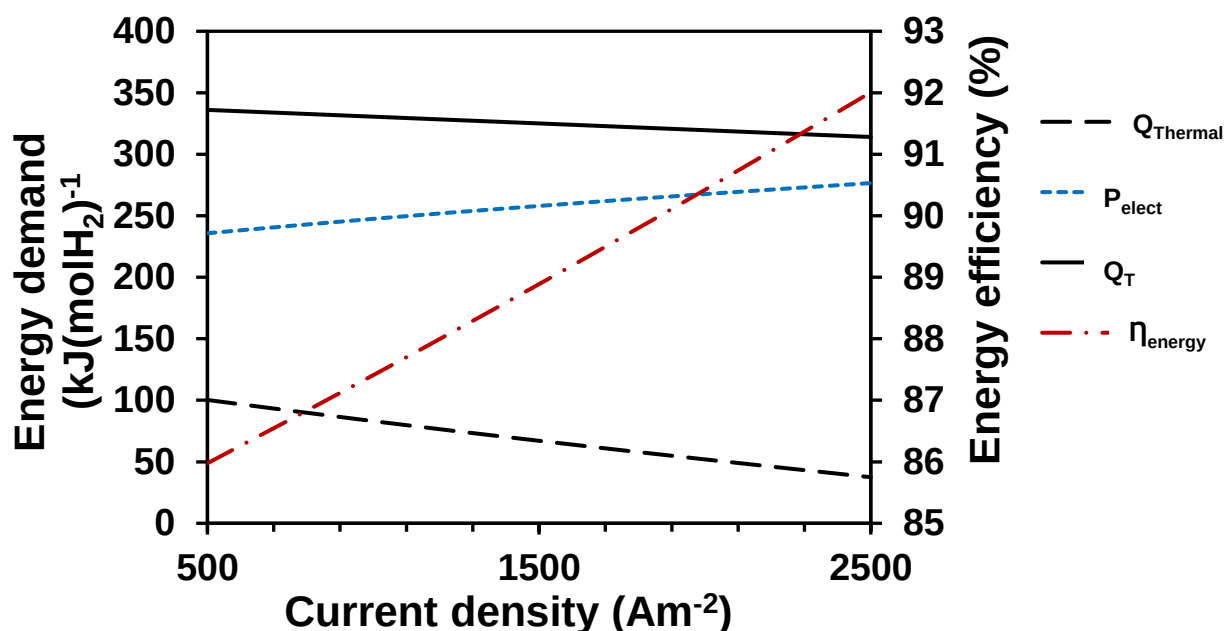


Figure 4.11: Influence of current density on the energy demand and the efficiency of the SOE

However, there is a decrease in thermal energy demand to about $38 \text{ kJ}(\text{molH}_2)^{-1}$, which may be due to the increased electrical energy demand driving the reaction kinetics, resulting in a higher rate of the reaction, and lowering the activation energy required for the electrolysis reaction and thus, a lower need for thermal energy. The combined effect of these changes results in a slight decrease in overall energy demand to $314 \text{ kJ}(\text{molH}_2)^{-1}$ at 2500 Am^{-2} and an increase in energy efficiency to 92%. These findings are in agreement with previous studies in the field that have reported similar trends in energy efficiency with increasing current densities in SOEs. For example, studies by Chen et al. (237) and Wang et al. (238) have shown that increasing the current density leads to higher energy efficiency due to improved reaction kinetics.

4.8 Optimisation

Optimising the operating parameters of a system is critical to improve its performance and efficiency. As mentioned earlier in the introduction section of this study, existing literature primarily relies on trial-and-error experiments to estimate the optimum values of operating parameters, which can be time-consuming and require a large number of experimental runs

especially for the multivariable operating parameters (239). To avoid this, a statistical design of experiments (DOE) approach, such as the Box-Behnken design (BBD), was used for the optimisation study. These approaches not only allow for the identification of optimal values, but also the identification of synergistic relationships between input parameters, making them a more efficient and effective method for optimising operating parameters. In general, for a second-order BBD, the general equation can be written as shown in Equation (4.27).

$$y = \beta + \sum_{i=1}^{\kappa} \beta_i a_i + \sum_{i=1}^{\kappa-1} \sum_{j=i+1}^{\kappa} \beta_{ij} a_i a_j + \sum_{i=1}^{\kappa} \beta_{ii} a_i^2 \quad (4.27)$$

Where y is the response variable, a_i and a_j are the independent variables or factors, β is the intercept term, β_i is the linear coefficient for the factor a_i , β_{ij} is the interaction coefficient for the pairs of factors a_i and a_j , and β_{ii} is the quadratic coefficient for the factor a_i . The coefficients in the model are obtained using the least squares regression (LSR) method. To facilitate the analysis, the levels of the true input factors (Z_i) are coded as a_i as reported by Tamilarasan and Renugambal (240) based on Equation (4.28).

$$a_i = \frac{Z_i - Z_0}{\Delta Z_i}, i = 1, 2, 3, \dots, N \quad (4.28)$$

Based on the BBD methodology, 46 sets of experiments were suggested for studying the five independent variables in this research. These variables include cell operating temperature (T) ranging from 650 to 900°C, steam-to-hydrogen feed ratio (FR) ranging from 25% steam to 90% steam, steam utilisation (U_{steam}) ranging from 60% to 95%, operating pressure (P) ranging from 1 to 20 bar, and current density (j) ranging from 500 to 2500 Am⁻². The responses considered in this study include the thermal energy demand ($Q_{Thermal}$), electrical energy demand (P_{elect}), and the total energy demand (Q_T), which are measured in kJ(molH₂)⁻¹.

4.8.1 Optimisation models development

The 46 sets of experiments were performed in the order suggested by the BBD methodology, using the developed Aspen Plus model of the SOE. This study also demonstrates one of the benefits of the developed SOE model, as it can conduct a large number of runs that would be challenging or expensive to carry out in an experimental or laboratory setting. The resulting data were used to generate optimisation models for each of the responses considered in this study, with the assistance of Minitab® 18. The models were based on the second-order BBD general equation, as shown in Equations (4.29) - (4.31).

Therefore, for thermal energy demand (Q_{Thermal}) in $\text{kJ}(\text{molH}_2)^{-1}$, we have:

$$\begin{aligned} Q_{\text{Thermal}} = & 394 + 0.283T - 1.015FR - 7.35U_{\text{steam}} - 0.86P - 0.0466j \\ & - 0.0003T^2 - 0.00079FR^2 + 0.01381U_{\text{steam}}^2 + 0.0917P^2 \\ & - 0.00000j^2 + 0.000675T(FR) + 0.00357TU_{\text{steam}} - 0.00231TP \\ & + 0.000054Tj + 0.00886FRU_{\text{steam}} - 0.00272FR(P) \\ & - 0.000081FR(j) - 0.0007U_{\text{steam}}P + 0.000094U_{\text{steam}}j \\ & - 0.000004Pj \end{aligned} \quad (4.29)$$

The electrical energy demand is given as:

$$\begin{aligned} P_{\text{elect}} = & 156 - 0.81T + 2.547FR + 6.58U_{\text{steam}} - 0.7P + 0.079j + 0.000708T^2 \\ & + 0.00132FR^2 - 0.00417U_{\text{steam}}^2 + 0.0057P^2 + 0.00j^2 \\ & - 0.000905T(FR) - 0.00355TU_{\text{steam}} + 0.00055TP - 0.000097Tj \\ & - 0.02668FRU_{\text{steam}} - 0.0008FR(P) + 0.000169FR(j) \\ & - 0.0006U_{\text{steam}}P - 0.000078U_{\text{steam}}j + 0.000006Pj \end{aligned} \quad (4.30)$$

For the total energy demand, it is given as:

$$\begin{aligned} Q_{\text{Total}} = & 550.2 - 0.527T + 1.532FR - 0.762U_{\text{steam}} - 1.56P + 0.0324j \\ & + 0.000408T^2 + 0.00052FR^2 + 0.00964U_{\text{steam}}^2 + 0.0974P^2 \\ & - 0.00j^2 - 0.000229T(FR) + 0.000025TU_{\text{steam}} - 0.00176TP \\ & - 0.000044Tj - 0.01783FRU_{\text{steam}} - 0.00347FR(P) \\ & + 0.000088FR(j) - 0.00133U_{\text{steam}}P + 0.000016U_{\text{steam}}j \\ & + 0.000002Pj \end{aligned} \quad (4.31)$$

The regression model for each response y was solved using the Desirability Function Approach (DFA). This technique employs a search-based optimisation strategy to fine-tune multiple

response variables. It does so on both individual and collective levels to identify the best optimal solution for the input variables (241). For minimising each response, the individual desirability function (d_i) were calculated using Equation (4.32). Where w is the weighted function, L_i denotes the lower boundary, T_i denotes the target value and y_i is the response variable.

$$d_i = \begin{cases} 1 & y_i < L_i \\ \left(\frac{T_i - y_i}{T_i - L_i}\right)^w & L_i \leq y_i \leq T_i \\ 0 & y_i > T_i \end{cases} \quad (4.32)$$

The most favourable result for the desirability function (d) or composite desirability function (D) is when it equals 1 or when it is close to 1.

4.8.2 Thermal energy demand optimisation

The optimal thermal energy demand of the SOE was determined using the regression model presented in Equation (4.29). The minimum thermal energy demand of the SOE was predicted to be $68.1 \pm 8.67 \text{ kJ}(\text{molH}_2)^{-1}$ at a 95% confidence level, with optimal values of 650 °C cell temperature, 90% steam in the steam-to-hydrogen feed ratio, 95% steam utilisation, 14.63 bar operating pressure, and 2500 Am^{-2} current density. The optimisation plot is illustrated in **Figure 4.12**.

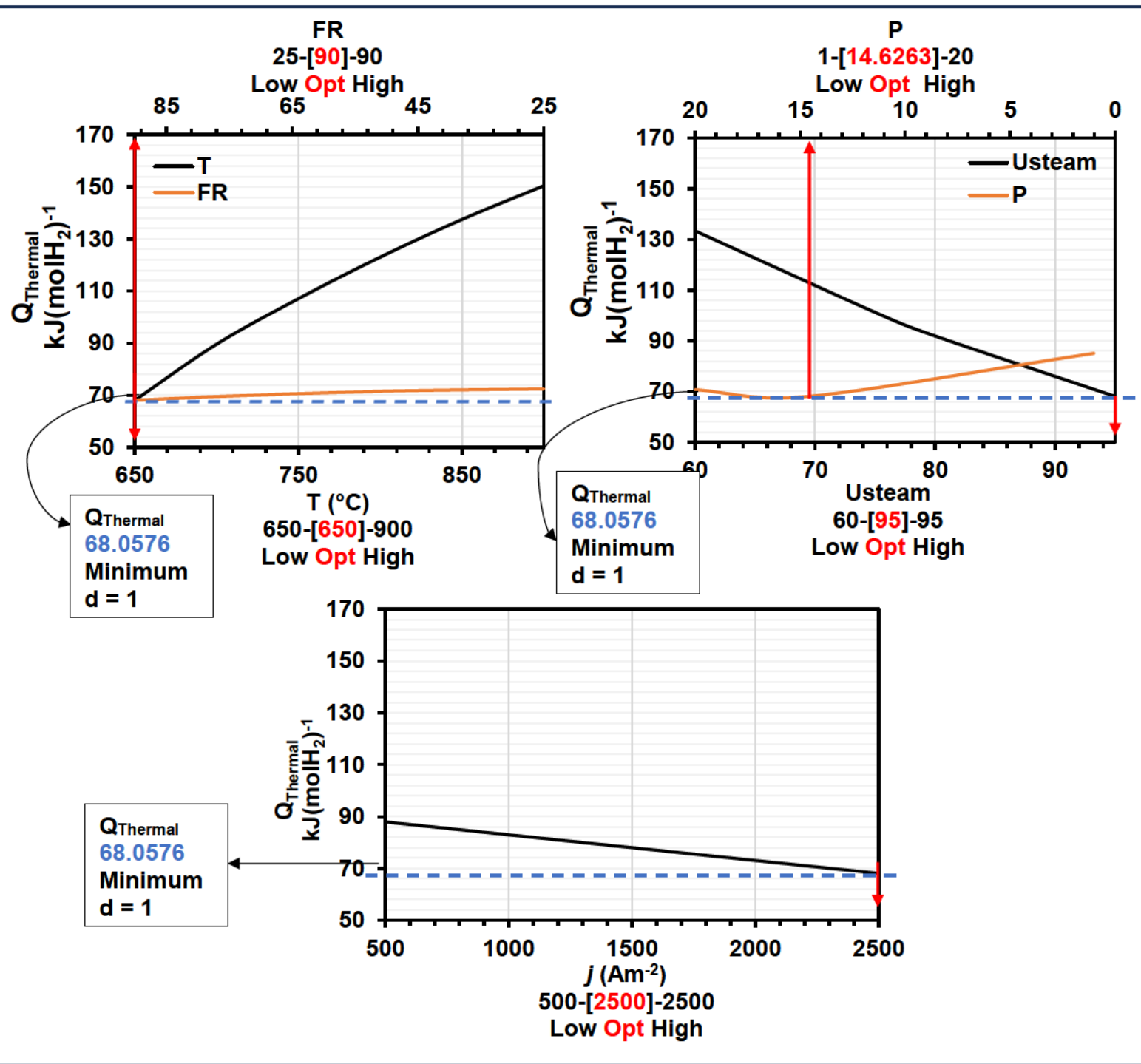


Figure 4.12: Optimisation plot for thermal energy demand (Q_{Thermal}) ($\text{kJ}(\text{molH}_2)^{-1}$)

4.8.3 Electrical energy demand optimisation

The regression model for the electrical demand, as shown in Equation (4.30), was used to estimate the minimum electrical energy demand of the SOE. The calculated electrical energy

demand was $170.1 \pm 14.6 \text{ kJ}(\text{molH}_2)^{-1}$ at a 95% confidence level, with optimal values of 900 °C cell temperature, 25% steam in the steam-to-hydrogen ratio, 60% steam utilisation, 20 bar operating pressure and 2500 Am^{-2} current density. The optimisation plot is shown in

Figure 4.13.

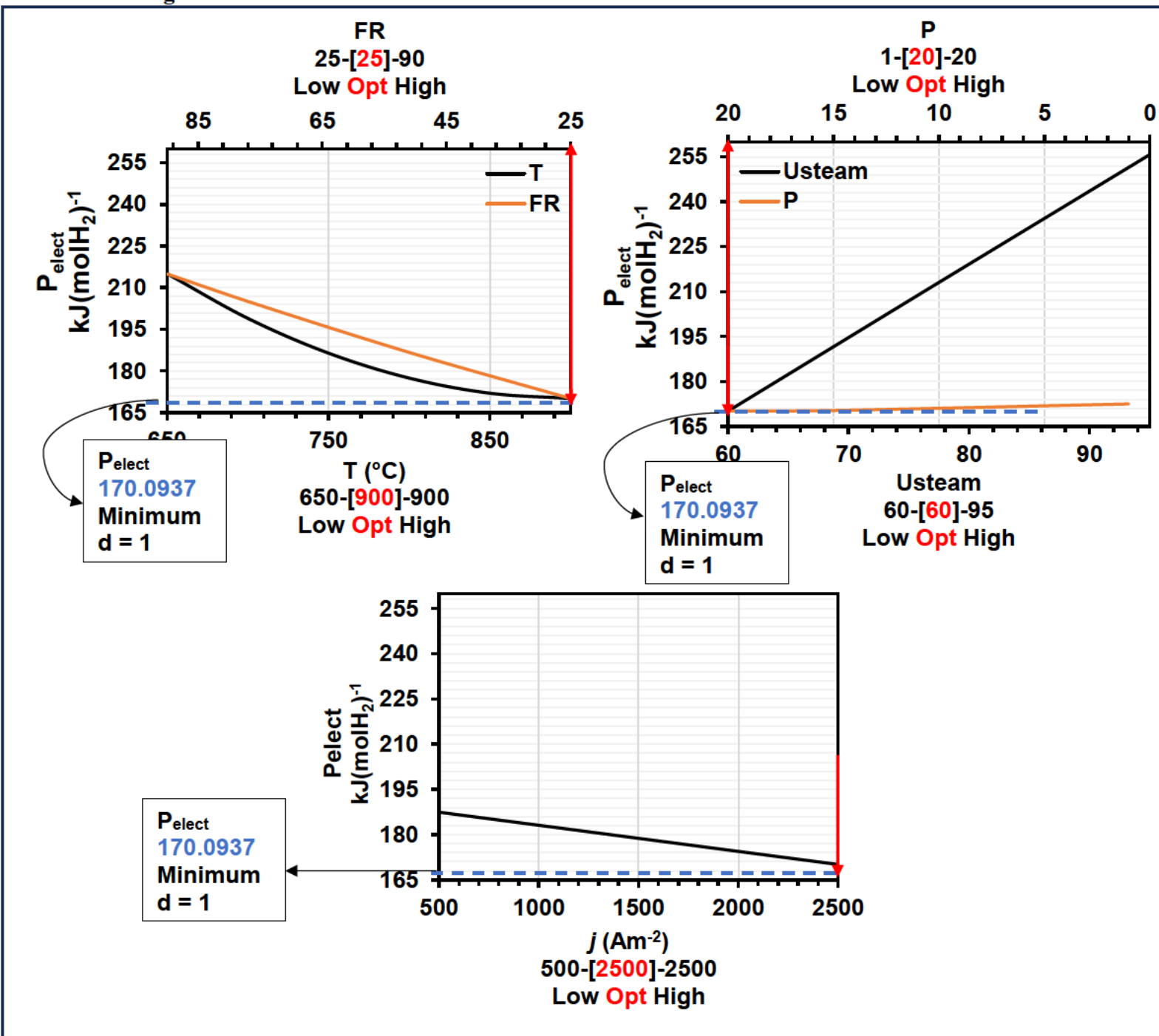


Figure 4.13: Optimisation plot for electrical energy demand (P_{elect}) ($\text{kJ}(\text{molH}_2)^{-1}$)

4.8.4 Total energy demand optimisation

The total energy demand of the SOE was minimised by using the quadratic regression model for the total energy demand (Equation (4.31)) to estimate the optimal set of factors within the investigated range.

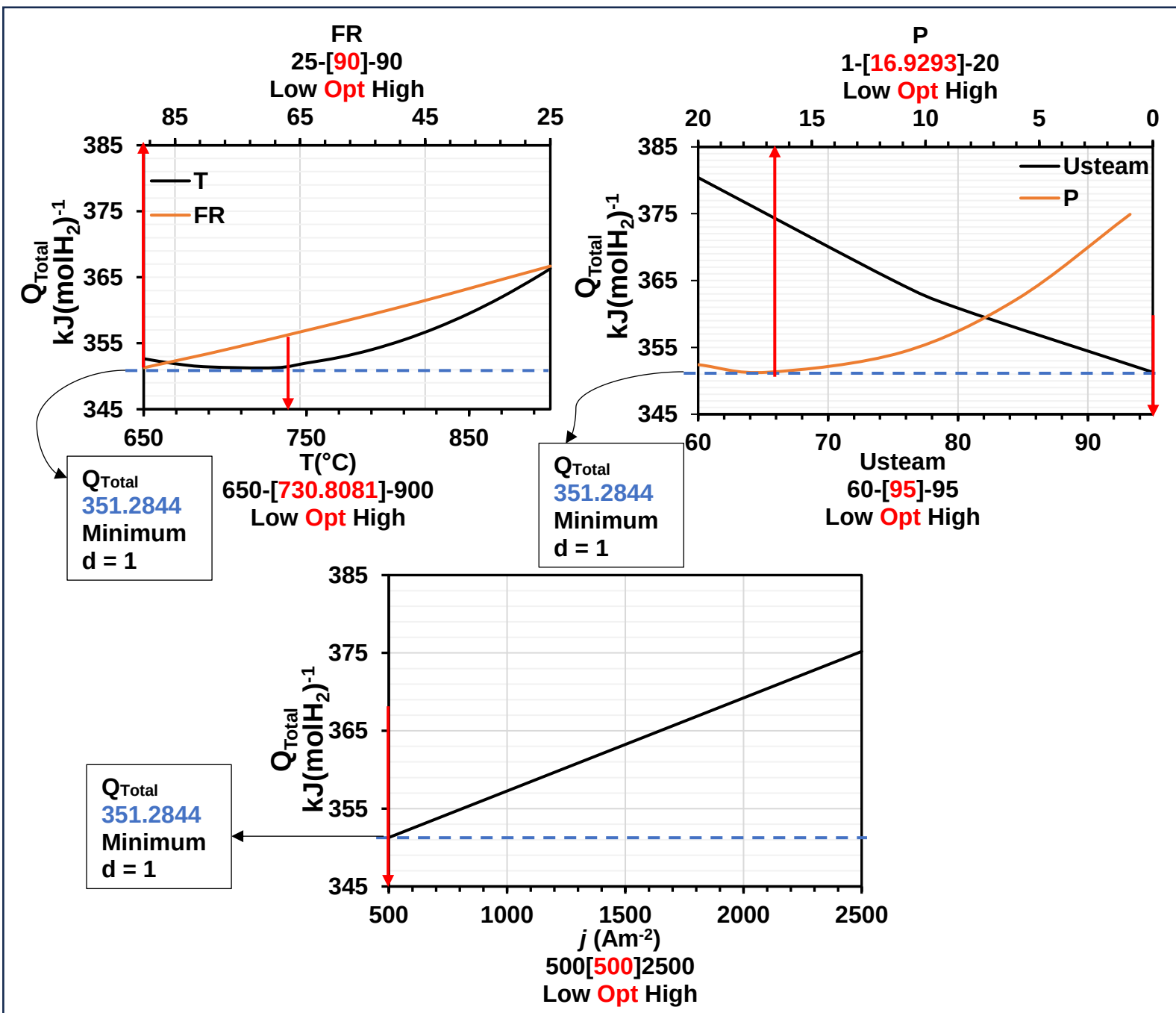


Figure 4.14: Optimisation plot for the total energy demand of the SOE (Q_T) ($\text{kJ}(\text{molH}_2)^{-1}$)
 1)

The predicted minimum total energy demand of the SOE was $351.3 \pm 3.93 \text{ kJ}(\text{molH}_2)^{-1}$ at a 95% confidence level. The optimisation plot is shown in **Figure 4.14**.

4.8.5 Multi-objective optimisation (MO)

For the multi-objective optimisation study, the Composite Desirability Function (CDF) approach was utilised to simultaneously optimise the thermal energy demand, electrical energy demand, and total energy demand of the SOE. The composite desirability (D) was determined by estimating the weighted geometric mean of all the individual desirability functions of the response of interest, using Equation (4.33). where, w_i is the scaling factor for each individual desirability value (d_i) corresponding to the i^{th} response, while n indicates the total number of responses. The best optimal solutions are determined by maximising the D, using a reduced gradient algorithm by using several initial points.

$$D = \prod_{i=1}^n d_i^{\frac{1}{w_i \sum_{i=1}^n w_i}} \quad (4.33)$$

The optimised values of $123.6 \pm 6.47 \text{ kJ}(\text{molH}_2)^{-1}$ for thermal energy demand, $228.7 \pm 8.87 \text{ kJ}(\text{molH}_2)^{-1}$ for electrical energy demand, and $352.3 \pm 3.86 \text{ kJ}(\text{molH}_2)^{-1}$ for total energy demand were obtained at a solution set of 781.3°C cell temperature, 90% steam in the steam-to- H_2 ratio, 95% steam utilisation, 17.5 bar operating pressure, and 500 Am^{-2} current density, with a composite desirability of 0.72 as shown in **Figure 4.15**. These results are reasonably consistent with the findings reported by Balta et al. (242) and Abdullah et al. (243). However, comparisons with literature results may be challenging due to differences in cell geometry, configurations, and inconsistencies in the other operating parameters of the steam SOE.

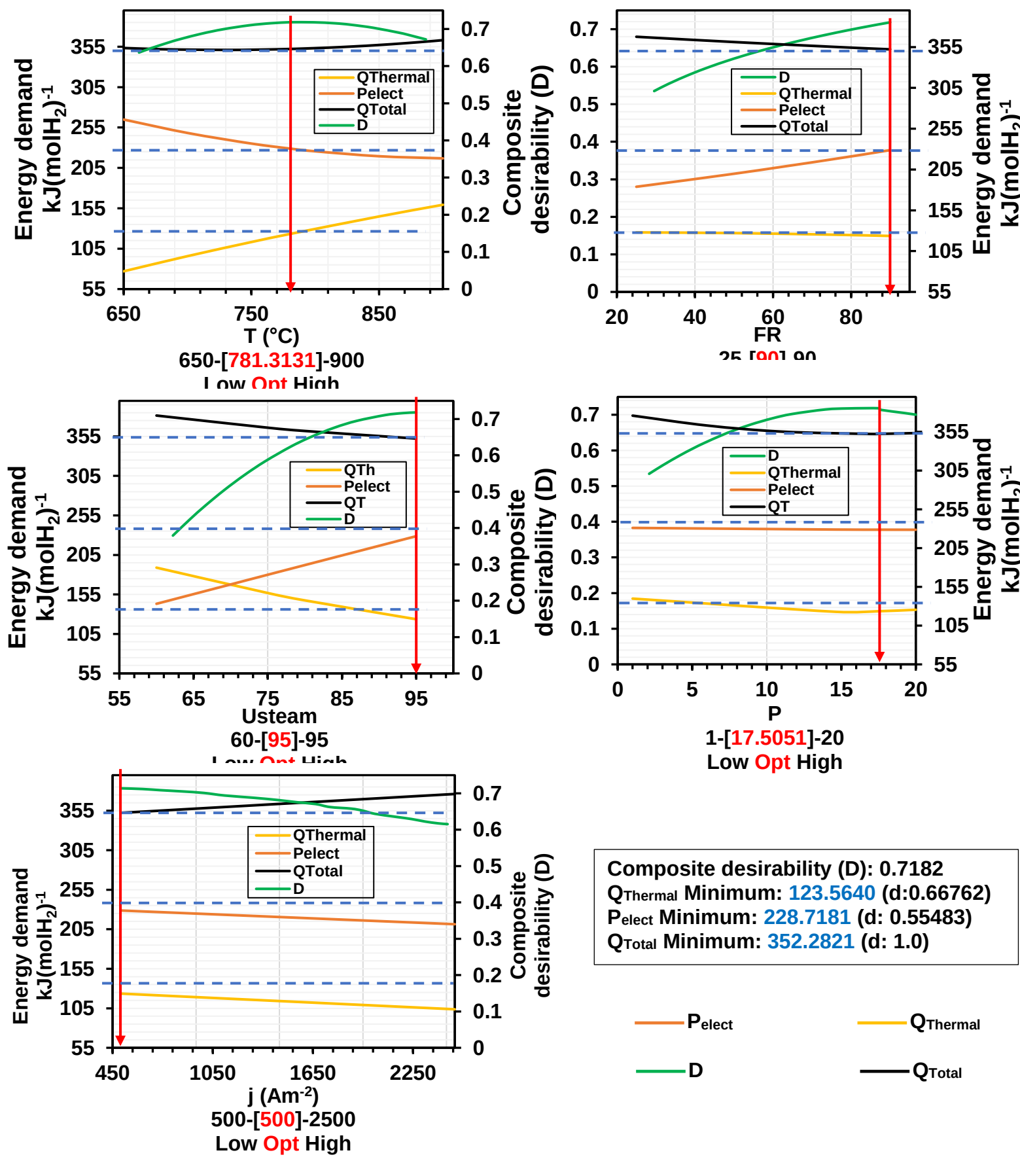


Figure 4.15: Multi-objective optimisation plot for the energy demands of the SOE

(kJ(molH₂)⁻¹)

4.8.6 Validation of optimal points

To validate the optimal model predictions of the thermal energy demand, electrical energy demand, and total energy demand of the SOE, as well as the multi-objective optimised points (MP), the simulated Aspen Plus model was utilised to run experiments for each case. **Table 4.4** presents the optimisation model predictions (OMP) and Aspen Plus model generated data (APMD) for all four optimal points. The maximum prediction error of 5.5% was observed for the predicted thermal energy demand values for the optimised solutions of total energy demand. These prediction errors are reasonably low, as 95% confidence intervals (CIs) were employed throughout the study. Therefore, a strong agreement was found between the Aspen Plus model generated data (APMD) and optimisation model predictions (OMP), indicating that the developed optimisation models can effectively be employed for predicting the energy demands of an SOE.

Table 4.4: The predicted thermal energy demand, electrical energy demand and total energy demand of the optimum level (mean $\pm$ 95 % CI) for both single and multi-objective optimal sets and corresponding Aspen plus model data (APMD)

Optimal conditions						Thermal energy demand (Q_{Thermal}) (kJ(molH ₂) ⁻¹)			Electrical energy demand (P_{elect}) (kJ(molH ₂) ⁻¹)			Total energy demand (Q_{T}) (kJ(molH ₂) ⁻¹)		
Objective function	T °C	FR (% steam)	U _{steam} (%)	P (bar)	j (A/m ²)	OMP	APMD	error (%)	OMP	APMD	error (%)	OMP	APMD	error (%)
Q_{Thermal}	650	90	95	14.6	2500	68.1 $\pm$ 8.7	67.2	1.3	312.0 $\pm$ 11.9	311.5	0.2	380.1 $\pm$ 5.2	378.7	0.4
P_{elect}	900	25	60	20	2500	195.9 $\pm$ 10.6	196.1	0.1	170.1 $\pm$ 14.6	176.8	3.8	366.0 $\pm$ 6.3	372.9	1.9
Q_{T}	730.8	90	95	16.9	500	112.5 $\pm$ 6.6	119.1	5.5	238.8 $\pm$ 9.0	234.0	2.1	351.3 $\pm$ 3.9	353.1	0.5
MP	781.3	90	95	17.5	500	123.6 $\pm$ 6.5	124.9	1.0	228.7 $\pm$ 8.9	230.3	0.7	352.3 $\pm$ 3.9	355.1	0.8

CHAPTER 5: MODELLING AND SIMULATION OF MOLTEN CARBONATE FUEL CELL FOR CO₂ CAPTURE

5.1 Introduction

To address the growing energy needs and environmental issues of climate change, it is essential to develop energy systems that utilise accessible fuel sources, demonstrate high performance, and have a minimal environmental footprint. Fuel cell systems are one potential answer to these challenges. Power plants based on fuel cells directly transform the chemical energy contained in fuels into electricity, bypassing the conversion of chemical energy to heat first, resulting in the well-known Carnot efficiency limitations. This leads to improved efficiency and reduced emissions of pollutants compared to conventional fossil fuel-powered energy conversion technologies. High-temperature fuel cells, such as MCFC and SOFC, show significant potential and have increasingly captured the interest of research and development efforts (244). Specifically, as they possess considerable flexibility towards using a range of fuels, from pure hydrogen to coal gas. The MCFC has demonstrated efficiencies between 50 and 60% (245) prior to heat recuperation and has primarily been employed for stationary electricity generation, accompanied by the generation of valuable heat. This makes it an appropriate choice for numerous industrial uses and decentralised power distribution.

MCFCs typically operate at around 650°C, a temperature necessary to achieve adequate ionic conductivity in the electrolyte (246). The elevated operating temperature enables the use of more cost-effective catalysts (such as Nickel instead of Platinum) and the potential integration of a gas turbine subsystem to enhance overall efficiency (247). Furthermore, MCFC can be employed for CO₂ separation (248) in fossil fuel power plants, making this technology highly attractive compared to the alternative methods. The MCFC employs a carbonate-based electrolyte, often a blend of lithium and potassium carbonate salts. These electrolyte materials

become molten at standard operating temperatures and are typically held in place and distributed over electrode surfaces via a ceramic electrolyte support mesh (commonly LiAlO_2). The anode materials are generally Ni-Cr/Ni-Al alloys, while the cathode materials consist of lithium-NiO.

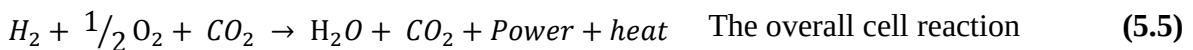
Numerous studies have been conducted on the modelling of MCFC in existing literature. For example, Michael et al. (245) developed a stack simulation model for a control study on direct reforming of MCFC power plants. The study demonstrated that there is a dependence of gas compositions on the slow reforming reaction rate, which is also a function of the stack temperature and regulated according to a large thermal time constant. Milewski et al. (249) investigated the performance of MCFC with respect to varying fuel and oxidant flow rates as a function of temperature by modelling a 100 cm² cell area MCFC. Umberto et al. (250) analysed the MCFC-based CO₂ capture system for small-scale combined heat and power (CHP) plants through modelling, discovering that a CO₂ removal efficiency of 63% was achieved with a corresponding total efficiency of approximately 35%. The system's output also includes thermal power due to the high temperature of the cathode exhaust off-gases, making it possible to consider integration with a cogeneration system. In comparison to other post-combustion CO₂ removal technologies, this system does not consume energy; rather, it generates additional electricity and thermal energy with an overall efficiency of about 70%.

In this study, a system-level simulation model of both external and internal reforming MCFC stacks is developed in AspenPlus™ as part of the ongoing decarbonisation integrated plants project. The development is based on the system-level features and first principle models, offering a detailed understanding of the MCFC system's mass/charge transport, thermodynamics, and heat transfer, that guide an MCFC and can easily be linked to other

subprocesses and at the same time allows the separate introduction of the oxidants. The simulation model was validated against published experimental data.

5.2 The Working Principles of Molten Carbonate Fuel Cell

The fundamental working principles of a molten carbonate fuel cell can be seen in **Figure 5.1** where, two porous electrodes make contact with a ceramic matrix saturated with molten carbonate salt, which acts as the electrolyte. Hydrogen gas, a fuel derived from hydrocarbon through steam reforming as illustrated in Equation (5.1) and (5.2), is supplied to the anode electrode, while the oxidant (a mixture of oxygen and carbon dioxide) is introduced at the cathode electrode. The oxygen and carbon dioxide in the oxidant stream react at the cathode electrode surface to generate carbonate ions (CO_3^{2-}) as shown in Equation (5.3). The matrix enables the ionic pathway for the CO_3^{2-} . The CO_3^{2-} then migrate through the electrolyte to the anode electrode. The Hydrogen gas in the fuel reacts with the CO_3^{2-} , producing steam and carbon dioxide as shown in Equation (5.4). For simplicity, both the cathode and anode reactions are combined into a single equation known as the overall cell reaction, and the stack convection losses as well as the useful DC electrical power are indicated as shown in Equation (5.5).



In general terms, as depicted in **Figure 5.1**, the electric current in an MCFC is produced from differences in partial pressures of oxygen and carbon dioxide between the cathode and anode sides. To achieve practical voltage values with a single cell, the oxygen partial pressure at the anode side must be low (10^{-19} bar), which can be attained by oxidising the fuel at the anode

side. The main operations of the MCFC, as seen in **Figure 5.1**, are often characterised by the appropriate ion and electron flows, which provide an equivalent electric circuit for the fuel cell.

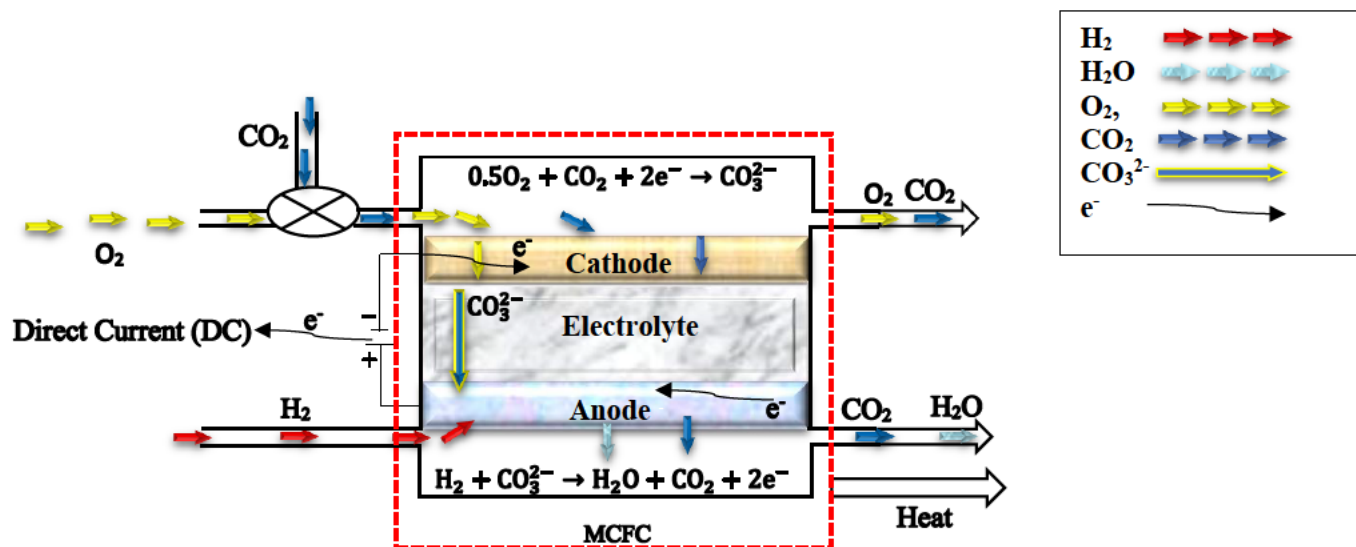


Figure 5.1: Fundamental operation of Molten Carbonate Fuel Cell

5.3 Simulations overview

The goal of the present study is to develop a detailed model of an MCFC model, utilising the commercially available AspenPlus™ software, to investigate the technical viability of combining the power plant's performance with carbon dioxide separation efficiency. The primary goal is to maximise power production while capturing a minimum of 65% of the carbon dioxide from the carbon dioxide source. Although the AspenPlus™ simulation package employed for the MCFC steady-state modelling in this study has been reported in several investigations for the modelling of fuel cell based power generation systems (251–256), there remain critical gaps in existing simulations. Specifically, previous models have not taken into account the separate introduction of O_2 and CO_2 from their original sources, a feature essential for a comprehensive understanding of the MCFC system's sustainability in real-world applications from potential economic considerations. Furthermore, the study offers simulations estimating the thermal energy released by the MCFC system, an aspect frequently neglected in existing literature.

The simulation begins with the development of the cell model as no MCFC model exist in the AspenPlus™ model library. However, the calculator block of the AspenPlus™ was used to interactively deliver the electrochemical computations needed for fuel cell modelling. The computation spreadsheet was configured based on mass balance equilibrium for an MCFC, while cell voltage was determined using Nernst's equation to compute open circuit voltage (OCV). The model inputs include temperature, pressure, and anode and cathode compositions and flow rates. Fuel cell operating parameters, such as pressure, temperature, cell area, and utilisation factors for fuel, oxygen, and carbon dioxide sources, are also required as inputs. The utilisation factors indicate the fuel, oxygen, and carbon dioxide fraction consumed within the cell as represented in Equation (5.10) - (5.11). The cell typically operates with an excess of these three components to ensure high performance and longevity. The outputs generated include current density, cell voltage, electrical power generated, thermal energy released, total flow rate of oxidants which include the Oxygen and carbon dioxide sources, and the composition of outlet flows. The AspenPlus™ model flowsheet developed in this study is depicted in **Figure 5.2**. Electrical power is generated as direct current (DC), with electrical energy efficiency and carbon dioxide removal efficiency defined by Equation (5.12) and (5.30), respectively. In the model, carbon dioxide removal efficiency aligns with the carbon dioxide utilisation factor.

5.3.1 Model flowsheet

Figure 5.2 shows the AspenPlus™ flowsheet of the MCFC stack. A concise description of the individual in-built models used in **Figure 5.2** is presented in **Table 5.1**. It shows the default IDs used in Aspen Plus model's library, IDs deployed in this study, and a brief explanatory note for each unit.

Table 5.1: Individual in-built models in in Aspen Plus used in the MCFC platform depicted in Figure 5.2

Default ID	Unit ID	Comment
Heater	HEATER	To maintain the same temperature between the electrodes
Sep	ELECTROL	Delivers electrochemically required amount of Oxygen and carbon dioxide to the anode.
Mixer	EJECTOR MIXER	To model mixing of the recycle stream and fresh fuel To model mixing of the CO ₂ and O ₂ source to form the oxidant for the MCFC cathode
RGibbs	ANODE	To model the electrochemical reaction of H ₂ and O ₂
Fsplit	REFORMER	To model the pre-reforming of the fuel
Heatx	SPLITTER	To model the splitting of the spent fuel
	CATHODE	To model the preheating of the incoming fresh oxidant

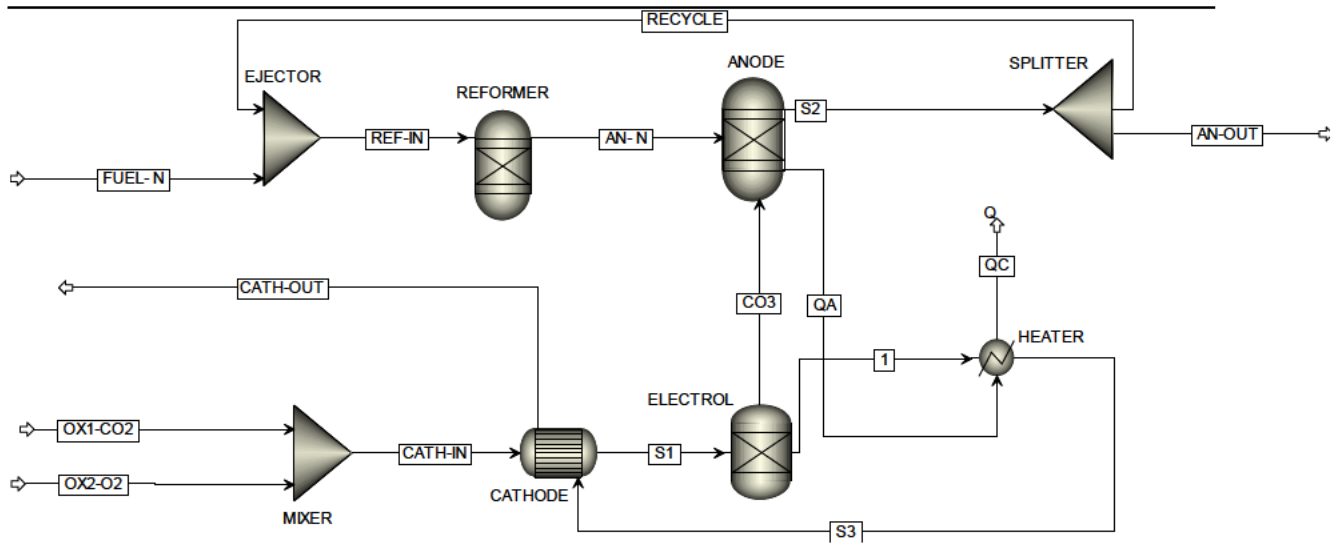


Figure 5.2: MCFC subsystem flowsheet

5.3.2 Detail assumption of the Simulation

The MCFC modelling employed in this study assumed the following theories

1. The model is of non-dimension.
2. The model ignore pressure drops across the unit operation blocks.
3. Simulation of ion movement is not feasible in Aspen plus, rather, Hydrogen oxidation reaction i.e., Equation (5.5) is taken into account.
4. All reactions observed chemical equilibrium criterion.

5. The model always assumed water gas shift reaction of Carbon monoxide to Hydrogen and steam reforming of Methane to Hydrogen if available in the fuel, so only Hydrogen is oxidised in the anode.
6. All operations are assumed to be on steady state and isothermal.
7. The fluids employed in the model obey the ideal gas law. (252,257,258).

5.3.3 Modelling and simulation of MCFC

As shown in **Figure 5.2**, the fuel stream 'FUEL-IN', which consists of the mixture of available fuel gas components (i.e. 20% H₂ and 80% CH₄, is fed into the 'EJECTOR' block to model the preheating of the fresh fuel and mixing of the recycle stream (mainly containing steam and carbon dioxide, with a fraction of unreacted hydrogen and carbon monoxide from downstream). The 'EJECTOR' block outlet stream 'REF-IN' is fed into the pre-reformer, where the fuel gas gets reformed according to Equation (5.1) and (5.2).

The stream 'AN-IN' from the 'REFORMER' is then fed to the 'ANODE' where oxidation of hydrogen takes place under specified operating conditions. The overall reaction shown in Equation (5.5) is considered in the anode to simulate the electrochemical reactions that take place in the MCFC.

The temperatures of both the input CO₂ source (i.e., flue gas or biogas), represented by the 'OX1-CO2' stream, and the O₂ source (i.e., air or pure oxygen), represented by the 'OX2-O2' stream, are specified, and mixed through a 'MIXER' block. The resulting outlet stream, named 'CATH-IN', is fed to the 'CATHODE' block, a heat exchanger that exchange heat between the incoming oxidant mixture and the cathode exit stream before the occurrence of the cathodic reactions. Afterward, the exit stream 'S1' is passed to the 'ELECTROL' block. In this block, the required number of moles of oxygen ($n_{O_2, \text{required}}$) and carbon dioxide ($n_{CO_2, \text{required}}$) for the hydrogen oxidation reaction are separated out by employing an Aspen Plus calculator block

using Equation (5.6) - (5.11) and fed to the 'ANODE' block through the 'CO3' stream to simulate the movement of the carbonate ion (CO_3^{2-}) through the electrolyte, as shown in **Figure 5.1**. Since ion movement modelling is not feasible in Aspen Plus, the overall cell reaction, as shown in Equation (5.5), was considered in the anode.

$$U_f = \frac{nH_{2,spent}}{nH_{2,in}} \quad (5.6)$$

$$nO_{2,required} = \frac{1}{2}nH_{2,spent} \quad (5.7)$$

$$nO_{2,required} = nO_{2,elect.trans} \quad (5.8)$$

$$nCO_{2,required} = nCO_{2,elect.trans} = nH_{2,spent} \quad (5.9)$$

$$U_{OX2-O_2} = \frac{nO_{2,required}}{n_{OX2-O_2} y_{O_2}} \quad (5.10)$$

$$U_{OX1-CO_2} = \frac{CO_{2,required}}{n_{OX1-CO_2} y_{CO_2}} \quad (5.11)$$

$$\eta_{CO_2,captured} = \frac{CO_{2,consumed}}{CO_{2,in}} \quad (5.12)$$

In Equation (5.6), $nH_{2,in}$ represents the molar flow rate of hydrogen available for the oxidation reaction in the anode of the MCFC. $nH_{2,spent}$ represents the molar flow rate of hydrogen consumed in the electrochemical oxidation reaction, and U_f represents the fuel utilisation factor of the MCFC, typically taking a value of 85%. In Equation (5.7) and (5.8), $nO_{2,required}$ represents the molar flow rate of oxygen required for the electrochemical reaction, while $nO_{2,elect.trans}$ simulates the molar flow rate of oxygen required to move through the electrolyte of the MCFC. If pure oxygen is used as the 'OX2-O2' stream, U_{OX2-O_2} as shown in Equation (5.10) represents the oxygen utilisation factor. However, if air is used as the 'OX2-O2' stream, U_{OX2-O_2} represents the air utilisation factor, where n_{OX2-O_2} is the inlet molar flow rate of the 'OX2-O2' stream and y_{O_2} is the mole fraction of oxygen in the 'OX2-O2' stream. $nCO_{2,elect.trans}$

in Equation (5.9) simulates the molar flow rate of carbon dioxide required to move through the electrolyte of the MCFC. $nCO_{2,required}$ represents the molar flow rate of carbon dioxide required stoichiometrically for the overall redox reaction in the MCFC. U_{OX1-CO_2} in Equation (5.11) represents the CO₂ source utilisation factor of the system, where n_{OX1-CO_2} represents the inlet molar flow rate of the CO₂ source at the MCFC cathode and y_{CO_2} represents the mole fraction of carbon dioxide in the CO₂ source. While $\eta_{CO_2,captured}$ in Equation (5.12) denotes the efficiency of CO₂ removal or captured, $CO_{2,consumed}$ represent the molar flow rate of CO₂ consumed in the electrochemical reaction and $CO_{2,in}$ is molar flow rate of CO₂ available in the CO₂ source.

However, the remaining unreacted component of the oxidant that forms the exit stream of the 'ELECTROL' block, namely '1', must be at the operating temperature of the system, which is 650°C, derived from the heat generated by the electrochemical reaction in the real plant/system. Nonetheless, this was modelled by directing a heat stream, named 'QA', from the 'ANODE' block to the 'HEATER' block, which is specified to operate at 650°C. The heat stream 'QC' simulates the overall thermal energy generated or released by the MCFC, which can be recaptured and used for the cogeneration process. The spent fuel stream, named 'S2', is fed to the 'SPLITTER' block, where it is divided into a 'RECYCLE' stream sent back to the 'EJECTOR' block and an 'AN-OUT' stream. The splitting ratio is calculated and adjusted using the design specification block until the desired steam-to-combustible carbon ratio of 5 to 2 (259) is achieved at the REFORMER block, as per the feed specifications. Similarly, the heated exit stream 'S3' from the cathodic side of the simulation flow diagram is fed to the heat exchanger named 'CATHODE' block as the hot-in stream to heat the incoming oxidant named 'CATH-IN' stream in the cathode. The hot-out stream exits the heat exchanger as the outlet cathode stream named 'CATH-OUT'.

5.4 The Electrical and Thermal Energy Released Computation

5.4.1 The Electricity Generated

The approach adopted for the computation of cell voltage in this study is the universally accepted Nernst model as the base equation for the reversible Nernst cell voltage V_{NST} , as shown in Equation (5.13), (5.14) and (5.15). This is coupled with voltage loss models which essentially model the irreversible losses caused by electrochemical dynamic limitations presented as resistive heating, mass transport limitations, or activation polarisation. These losses are captured by local computation of the three main core losses, which include Ohmic, concentration, and activation polarisations (246).

$$V_{NST} = E^0 + \frac{RT}{n_e F} \ln\left(\frac{P_{H_2, Anode} P_{O_2, Cathode}^{\frac{1}{2}} P_{CO_2, Cathode}}{P_{H_2O, Anode} P_{CO_2, Anode}}\right) \quad (5.13)$$

$$P_{i, Anode} = \frac{x_{i, Anode} P_{Anode}}{P_{atm}} \quad (5.14)$$

$$P_{i, Cathode} = \frac{x_{i, Cathode} P_{Cathode}}{P_{atm}} \quad (5.15)$$

$$E_0 = 1.2723 - 2.7645 \times 10^{-4} T \quad (5.16)$$

Where, P_i denotes the partial pressure of the specie i , $x_{i, Anode}$ denotes the mole fraction of the specie i at the anode, $x_{i, Cathode}$ denotes the mole fraction of the specie i at the cathode and P_{atm} denotes the atmospheric pressure.

5.4.2 Voltage loss models

Polarisation losses are typically influenced by cell temperature, current density, and reacting species' partial pressures, which are all spatially dispersed inside a real-life cell. The literature presents a number of methods for estimating these polarisation losses. An approach is to use the Butler-Volmer equation to obtain the activation polarisation and the concentration polarisation. According to this approach, the equations for activation, concentration, and Ohmic polarisation are as follows (227) as shown in Equation (5.17) - (5.19).

$$R_{ohm} = jR_{int} \quad (5.17)$$

$$Z_{conc} = \frac{RT_{avg}}{\alpha n_e F} \ln \left(1 - \frac{j}{Aj_l} \right) \quad (5.18)$$

$$Z_{act} = \frac{RT_{avg}}{\alpha n_e F} \ln \left(\frac{j}{Aj_0} \right) \quad (5.19)$$

where A is the cell area, j_l is the fuel cell's limiting current density, which is affected by the transport phenomena that take place in the fuel cell electrodes; j_0 and R_{int} is the cell exchange current density, and internal resistance respectively. Since the literature suggest that the exchange current density j_0 is influenced by the cell operating temperature and pressure of the fuel cell, the formula for j_0 , according to Bessette's work (260), could be expressed as $j_0 = a + bT$. However, the mere dependency of j_0 on the operating temperature of the cell, according to experimental evidence, is inadequate. Earlier studies by Rivera cited in (246) suggested that the equation $j_0 = a + bT + cP + dPT$ may be used to estimate the value of exchange current density. j_0 values range from 10 to about 2500 Am² for a temperature and pressure range of 590 to 650 °C and 1-3 atm, respectively. According to Larminie and Dicks (261), this falls within a tolerable range. These values were obtained by employing a transfer coefficient (α) of 0.5.

Yuh and Selman (262,263) proposed a different strategy that has gained considerable support. This strategy combines a generic, macro-homogeneous theory of the active reaction sites (agglomerates) with a, micro-geometric model of the gas transport and current conduction in the electrode. In this "agglomeration model," the porous electrode is spatially separated into two regions: one with macro-pores and the other with agglomerates of solid particles with liquid-filled micro-pores, which forms the basis employed in the study.

Therefore, the energy losses considered in this model include the Cell ohmic or internal resistance given by (264) from Arrhenius equation as shown in Equation (5.20), the

concentration and activation polarisation that occur at the anode and cathode given by (263) as shown in Equation (5.21) and (5.22) respectively.

$$R_{ohm} = 0.45 \times 10^{-5} \exp \left[8600 \left(\frac{1}{T_{avg}} - \frac{1}{923} \right) \right] \quad (5.20)$$

$$Z_{Anode} = 2.27 \times 10^{-9} \exp \left[\frac{E_{act,an}}{RT_{avg}} \right] P_{H_2}^{-0.42} P_{CO_2}^{-0.17} P_{H_2O}^{-1.0} \quad (5.21)$$

$$Z_{Cathode} = 7.505 \times 10^{-10} \exp \left[\frac{E_{act,cath}}{RT_{avg}} \right] P_{O_2}^{-0.43} P_{CO_2}^{-0.09} \quad (5.22)$$

and

$$T_{avg} = \frac{(T^s + T_c^{in})}{2} \quad (5.23)$$

$$P_{i,Cat_loss} = \frac{P_{Cathode}^s (x_{i,Cathode}^s + x_{i,Cathode}^{in})}{2} \quad (5.24)$$

$$P_{i,An_loss} = \frac{P_{Anode}^s (x_{i,Anode}^s + x_{i,Anode}^{in})}{2} \quad (5.25)$$

Where, R_{ohm} denotes the cell ohmic or internal resistance, Z_{Anode} denotes the concentration and activation polarisation occurring at the anode, $Z_{Cathode}$ denotes the concentration and activation polarisation occurring at the cathode, T_{avg} denotes the arithmetic average of cathode inlet and exit temperature (k), T^s denotes the exit temperature (k) of the cathode, T_c^{in} denotes the inlet temperature (k) of the cathode, P_{i,Cat_loss} denotes the partial pressure of the specie i at the cathode for energy loss, P_{i,An_loss} denotes the partial pressure of the specie i at the anode for energy loss, $x_{i,Cathode}^s$ denotes the mole fraction of the specie i at the cathode exit and $x_{i,Cathode}^{in}$ denotes the mole fraction of the specie i at the cathode inlet.

Voltage loss (V_{loss}) therefore take the form as shown in Equation (5.26):

$$V_{loss} = j(R_{ohm} + Z_{Anode} + Z_{Cathode}) \quad (5.26)$$

Where, j denotes the cell current density.

Therefore, the actual MCFC cell voltage (V_{MCFC}) was determined by subtracting the various losses discussed above from the Nernst reversible voltage as shown in Equation (5.27).

$$V_{MCFC} = V_{NST} - V_{loss} \quad (5.27)$$

The cell current (I_{mcfc}) in ampere was determined from the Equation (5.28) where $\dot{n}_{H_2}$ indicates the molar flow rates of hydrogen consumed, and n_e here denotes the number of moles of electrons released per mole of Hydrogen consumed.

$$I_{mcfc} = n_e F \dot{n}_{H_2} \quad (5.28)$$

The electrical power $P_{elect,mcfc}$ released by the MCFC is calculated from Equation (5.29).

$$P_{elect,mcfc} = I_{mcfc} \cdot V_{MCFC} \quad (5.29)$$

$$\eta_{P_{elect,mcfc}} = \frac{P_{elect,mcfc}}{\dot{n}_{fuel} \cdot LHV_{fuel}} \quad (5.30)$$

Where $\eta_{P_{elect,mcfc}}$ is the electrical power efficiency, $\dot{n}_{fuel}$ denotes the molar flow rate of fuel (mols⁻¹), and LHV_{fuel} represent the lower heating value of the fuel used.

5.4.3 The Thermal Energy Generated

Some fraction of the chemical energy contained in the fuel is converted into power by the MCFC; the remaining fraction will be converted to heat as a result of system losses. The preheating of the incoming fresh fuel, oxygen, and carbon dioxide source streams uses some of this heat, but the endothermic reforming reaction consumes considerable amounts of it. The "ANODE" block model's net heat duty (QA) is calculated in AspenPlus™ using the Equation (5.31):

$$QA = Q_O + Q_S + Q_W - Q_I \quad (5.31)$$

where Q_O , Q_S , and Q_W are the heat of reaction for reactions in Equation (5.1) to (5.5) specified in the "ANODE" block, respectively and Q_I is the initial heat of the fresh fuel, oxygen, and carbon dioxide source streams. Consequently, the value for the thermal energy ($Q_{Th,mcfc}$) released by the MCFC is taken from the heat stream 'QC', which is the resultant heat released after heating the cathode compartment, as explained in the previous section titled '**Simulation**' and as shown in Equation (5.32).

$$Q_{Th,mcfc} = QC = QA - Q_{CATHODE} \quad (5.32)$$

5.5 Model Validation

The model was validated against a set of experimental data obtained from (246), who explored the discrepancy between an agglomerate model and a simplified model against the results obtained from laboratory experiments at different cell operating temperatures (i.e. 590 to 650 °C) to ensure its flexibility and applicability to real-life plant configurations. In the study, a cell with a 0.01 m² planar area was used. The experimental setup involved cells placed between separator plates, which were engineered with 21 channels, each measuring 3mm in width and height for the cathode, and 3mm in width and 1.5mm in height for the anode. A fuel stream containing 60% hydrogen, 15% carbon dioxide, and 25% steam, along with an oxidant stream containing 8% carbon dioxide, 25% steam, 59% nitrogen, and 8% oxygen, flows simultaneously in opposite channels. The electrode-electrolyte matrix is situated between two opposing separator plates. Other operating parameters used for model validation, as reported in the experiment, are presented in **Table 5.2**. For validation purposes, the model cell current is input manually, and the model determines the molar flow rate of the fuel. Consequently, **Figure 5.3** and **Figure 5.4** display the model predictions and experimental I-V curves, respectively, for two different cell operating temperatures (590 and 650 °C).

Table 5.2: Input data for the model validation

Parameter	Values
Fuel gas composition (%)	H ₂ (60), CO ₂ (15) and H ₂ O (25)
Oxidant gas composition (%)	O ₂ (8), N ₂ (59), CO ₂ (8) and H ₂ O (25)
Operating pressure (atm)	1 – 3
Area of active site (m ²)	0.01
Operating temperature (°C)	590 - 650
Limiting current density (A m ⁻²)	4000
Transfer coefficient (-)	0.5
Fuel utilisation factor (U _f) (-)	0.85
Cathode activation energy (kJ kmol ⁻¹) at 1 atm	102800
Cathode activation energy (kJ kmol ⁻¹) at 2 atm	99000
Cathode activation energy (kJ kmol ⁻¹) at 3 atm	93000
Anode activation energy (kJ kmol ⁻¹)	53500

The polarisation curves, which depict the voltage-current characteristics of the electrochemical reactions within Molten Carbonate Fuel Cells (MCFCs), provide valuable insights into their performance (261). **Figure 5.3** and **Figure 5.4** illustrate the experimental and predicted current-voltage (I-V) curves at temperatures of 590 °C and 650 °C, respectively, for three different operating pressures (1, 2, and 3 atm). These plots primarily focus on the kinetically dominated region of the MCFC, characterised by low current density.

At 590 °C, the maximum relative error in voltage between the experimental data and the model predictions is approximately 3% observed at an operating pressure of 2 atm. The highest correlation coefficient (0.999) is achieved at 3 atm.

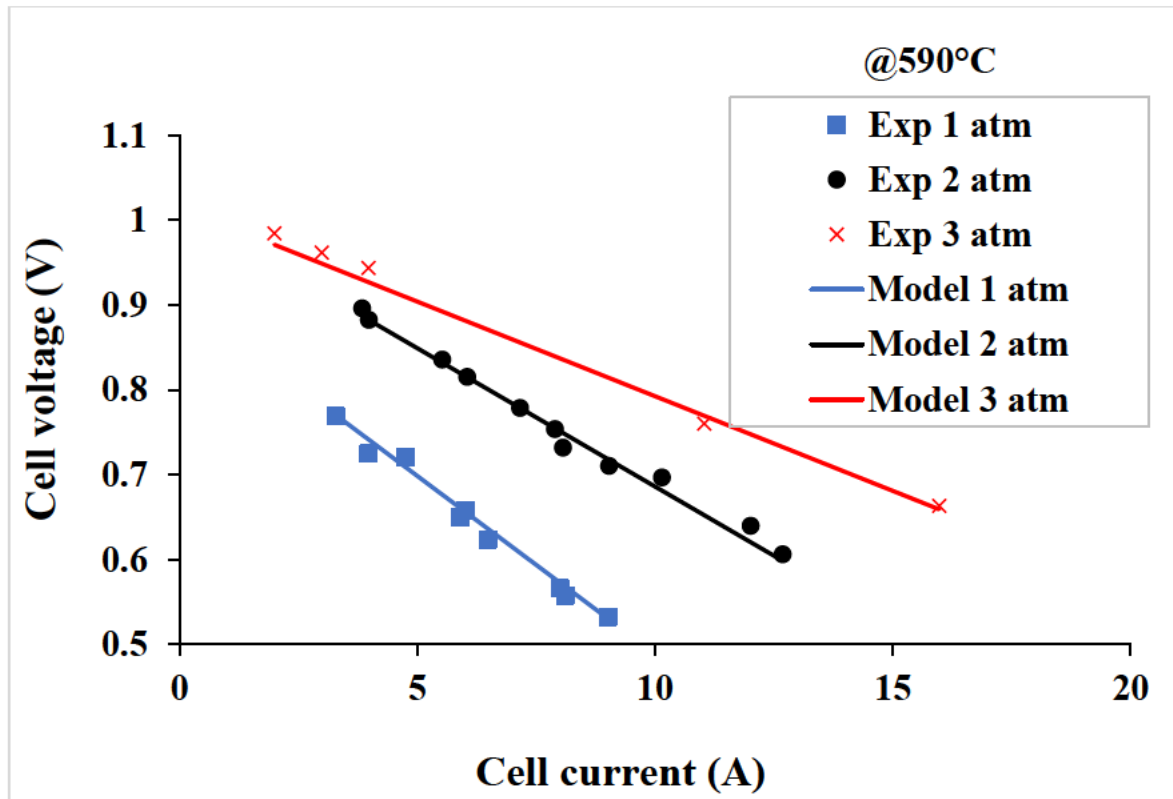


Figure 5.3: Model prediction and experimental I-V curves at cell operating temperature of 590°C and operating pressure of 1 - 3 atm (Experimental data obtained from (246))

In contrast, at a temperature of 650 °C (Figure 5.3), the maximum relative error decreases to 0.9% at an operating pressure of 3 atm. The correlation coefficient remains consistently high at 0.999 across all investigated pressure levels, signifying that the model closely corresponds with experimental results.

From a statistical standpoint, the model demonstrates strong performance in predicting the I-V characteristics of MCFCs. The maximum relative errors are consistently below 3%, and the correlation coefficients are consistently high, above 0.994 for the various temperature and pressure conditions investigated. However, the model's performance is generally better at higher temperatures (650 °C), with lower relative errors in the predictions.

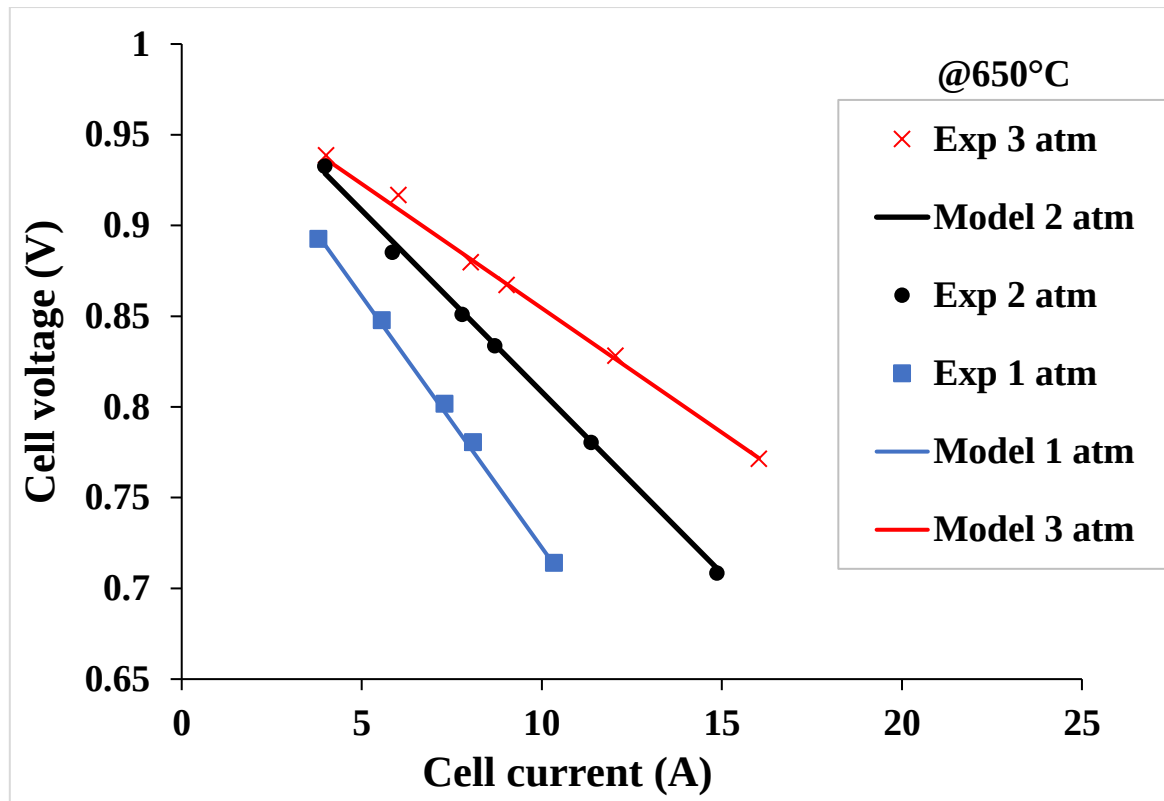


Figure 5.4: Model prediction and experimental I-V curves at cell operating temperature of 650°C and operating pressure of 1 - 3 atm Experimental data obtained from (246).

Therefore, the MCFC model demonstrates a high degree of accuracy in predicting I-V curves across different temperature and pressure conditions. The strong correlation coefficients and relatively low relative errors indicate the model's potential for informing the design and operation of MCFC systems.

5.6 Results and discussions

The validated model offers capabilities that were used to conduct several interactive system level analyses. In contrast to the existing models, the current model offers computational features. An example is its capability to estimate the thermal energy released by the MCFC that is crucial in evaluation of the whole decarbonisation system. Additionally, this model enables the exploration of oxidant sources, as O_2 and CO_2 are supplied separately, representing a significant improvement over many of previous models.

5.6.1 Sensitivity Analysis: Effect of fuel utilisation factor

The fuel utilisation factor (U_f) is a critical operating parameter for fuel cells. It affects the proportion of unspent fuel in the exit stream of the anode, which is an outcome of conversion efficiency, but is also of vital importance when targeting CO₂ capture techniques (250). **Figure 5.5** shows the effect of U_f on the power-to-heat ratio, cell voltage, and the DC electricity output efficiency of an MCFC at a constant fuel input flow rate of 6.6 kmol/hr and S/C ratio of 2.5.

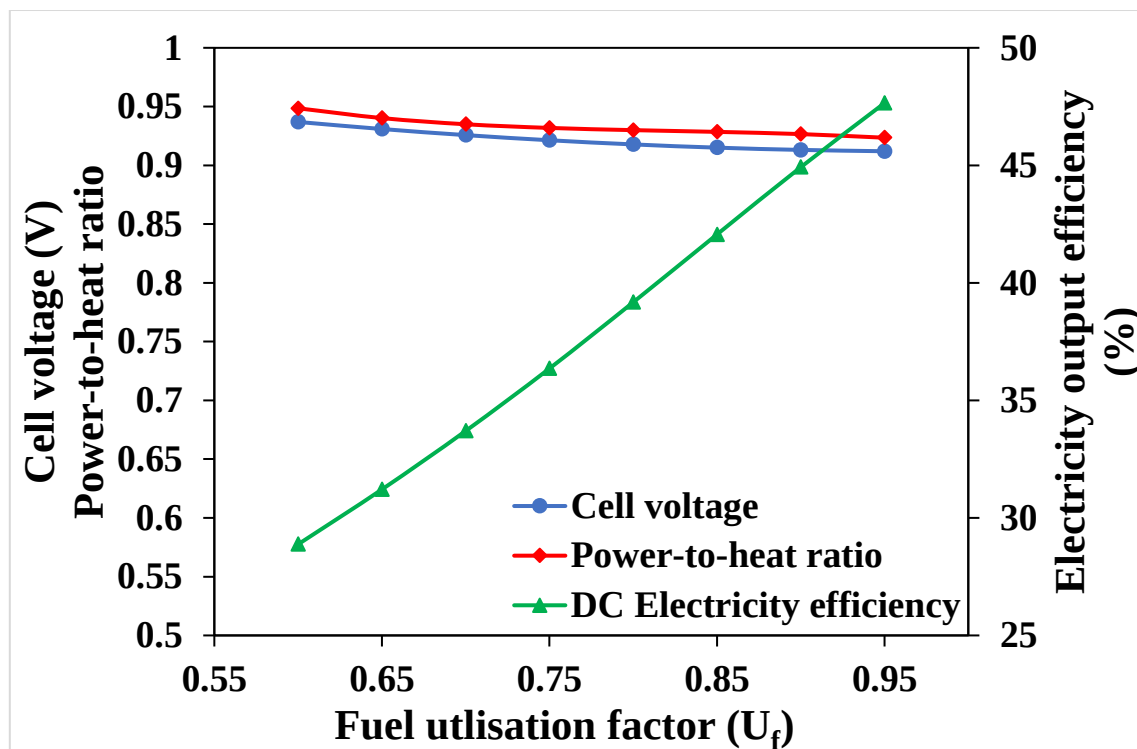


Figure 5.5: Effect of fuel utilisation factor (U_f) on the cell voltage, power-to-heat ratio, and the DC electricity efficiency at S/C ratio of 2.5

A subtle decrease in cell voltage is observed with the U_f , which can be attributed to the reduced average reactant concentration across the cell, i.e. concentration polarisation which consequently reduces the Nernst voltage at a higher level of fuel depletion.

The power-to-heat ratio experiences a slight decline, as the generation of heat increases with current density achieved by the increased flow rate of consumable hydrogen. The electrical efficiency rose approximately 65% across the investigated U_f range (from ~28% to ~48%).

This can primarily be attributed to the decreased recirculated fuel flow rate at higher U_f . The captured trends for various variables are in a good agreement with data reported in the literature (249,265).

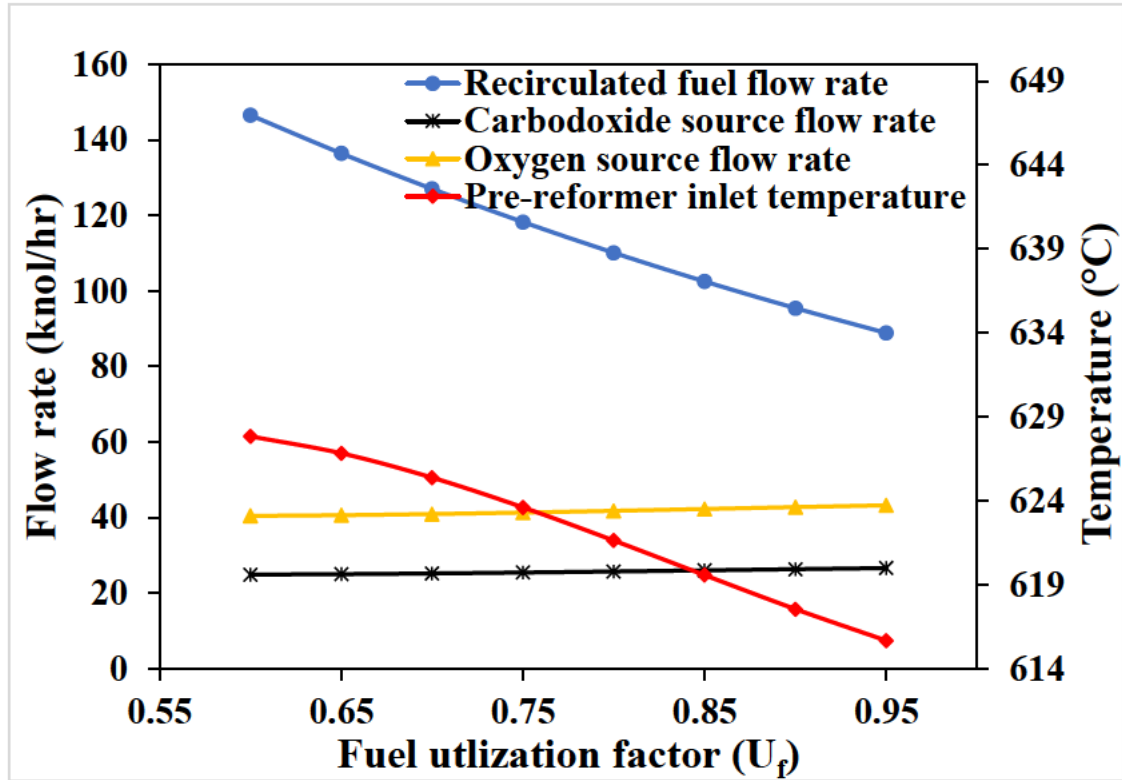


Figure 5.6: Effect of fuel utilisation factor (U_f) on the recirculated fuel flow rate, carbon dioxide source flow rate, oxygen source flow rate and pre-reformer inlet temperature

For instance, a study conducted by Kimihiko et al., (183) found a similar trend between higher U_f s and improved electricity output efficiency and a decrease in cell voltage.

As can be seen in **Figure 5.6**, the flow rate of recirculated fuel reduces by U_f , as a lower flow rate of fuel required for recirculation to maintain the predetermined S/C ratio, due to the higher steam content present in the spent fuel. Consequently, with less high-temperature exhausted fuel being recirculated, the pre-reformer's temperature drops.

The U_f dominates the anode exhaust composition. This model presented in the current work is developed for future application in simulating a comprehensive power-to-gas energy system plant, where the anode exit stream's dry composition will contribute a portion of the stream

directed to the methanator for methane generation. Based on the stoichiometry of the methanation reaction, it is necessary to have a hydrogen-to-carbonmonoxide ratio of 3:1 or a hydrogen-to-carbondioxide ratio of 4:1 to achieve optimal methane production in the methanator.

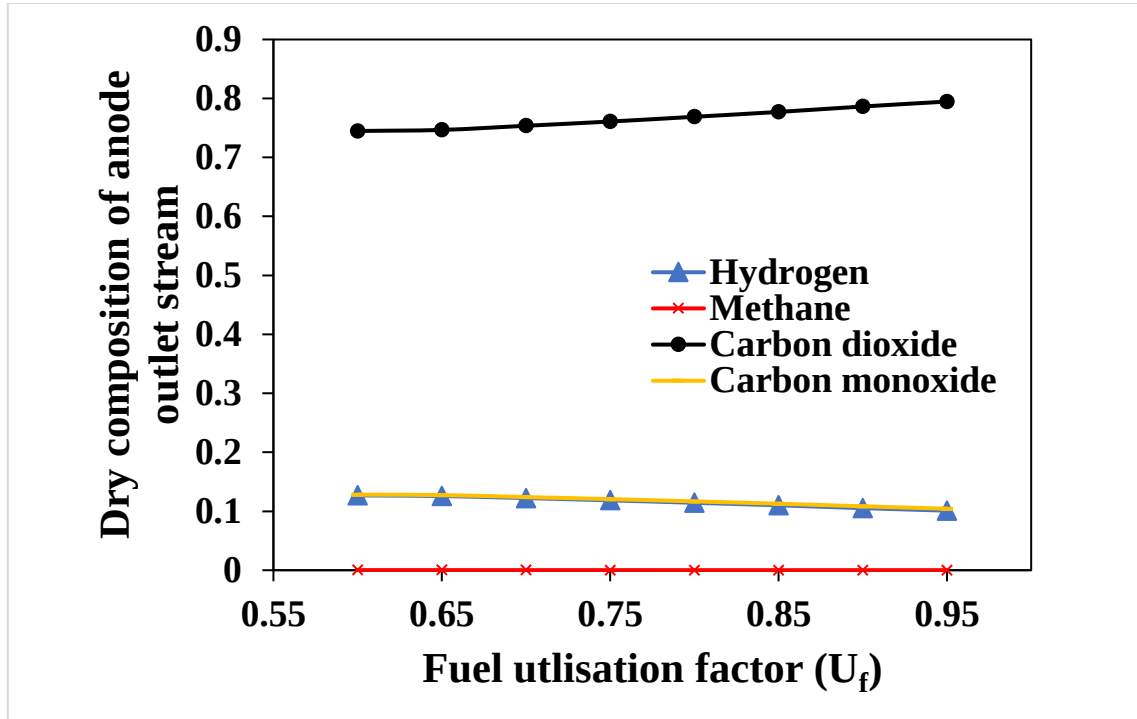


Figure 5.7: Effect of fuel utilisation factor (U_f) on the composition of anode exit stream on the dry basis

As a result, the mole fractions of CO, H₂, and CO₂ in the anode exit stream hold considerable interest. **Figure 5.7** shows that the CO₂ concentration at the anode exit stream increases with an increase in the U_f due to more depleted fuel, leading to reduced concentrations of CO and H₂. When U_f attains a value of 0.95, the CO₂ concentration stands at 79.5%, while H₂ and CO concentrations are at 10.1% and 10.4% (all molar and on a dry basis), respectively. However, it should be noted that the results in this study are influenced by the input fuel composition consisting of 80% CH₄ and 20% H₂, along with pure CO₂ as 'OX1-CO2' and pure O₂ as 'OX2-O2'.

CHAPTER 6: COUPLING OF A MOLTEN CARBONATE FUEL CELL WITH A SOLID OXIDE ELECTROLYSIS CELL FOR BIOGAS AND FLUE GAS DECARBONISATION: FEASIBILITY STUDY AND PROCESS EFFECTIVENESS

6.1 Introduction

As global energy demand rises alongside net-zero carbon targets, renewable energies like biomass, which contributes 8.3% (266) of total renewable energy, are crucial for sustainable and clean electricity generation. Biogas, a key renewable fuel, significantly reduces carbon emissions while supporting clean and sustainable electric power production without the release of fossil carbon (267).

Biogas, consisting mainly of methane and carbon dioxide, requires pre-treatment before injection into the natural gas grid. By cleaning and upgrading, raw biogas is transformed into biomethane, a product equivalent to natural gas with 95% and higher methane content. Biomethane can be used interchangeably or mixed with natural gas in various applications, including domestic appliances, cogeneration plants, fuel cells, commercial/industrial equipment, and CNG refuelling stations (268).

Europe is a world-leading producer of biomethane, and the EU promotes the use of biogas as a sustainable energy source. Directive 2009/73/EC (269,270) requires non-discriminatory access to the natural gas grid from Member States, but grid injection is conditional upon meeting gas quality requirements and safety standards. In most European countries, biomethane quality must meet local requirements, meaning the heating value and Wobbe index must be adapted to natural gas conditions. Natural gas in Europe is divided into high calorific (group H) and low calorific (group L) gases, with gas from the North Sea often being L quality and Russian gas being H quality. The Wobbe index of biomethane can be increased by adding propane and/or butane. The upgrading process (**Figure 6.1**) can be controlled to produce biomethane that meets predetermined quality standards (268,271). Cleaning processes, which

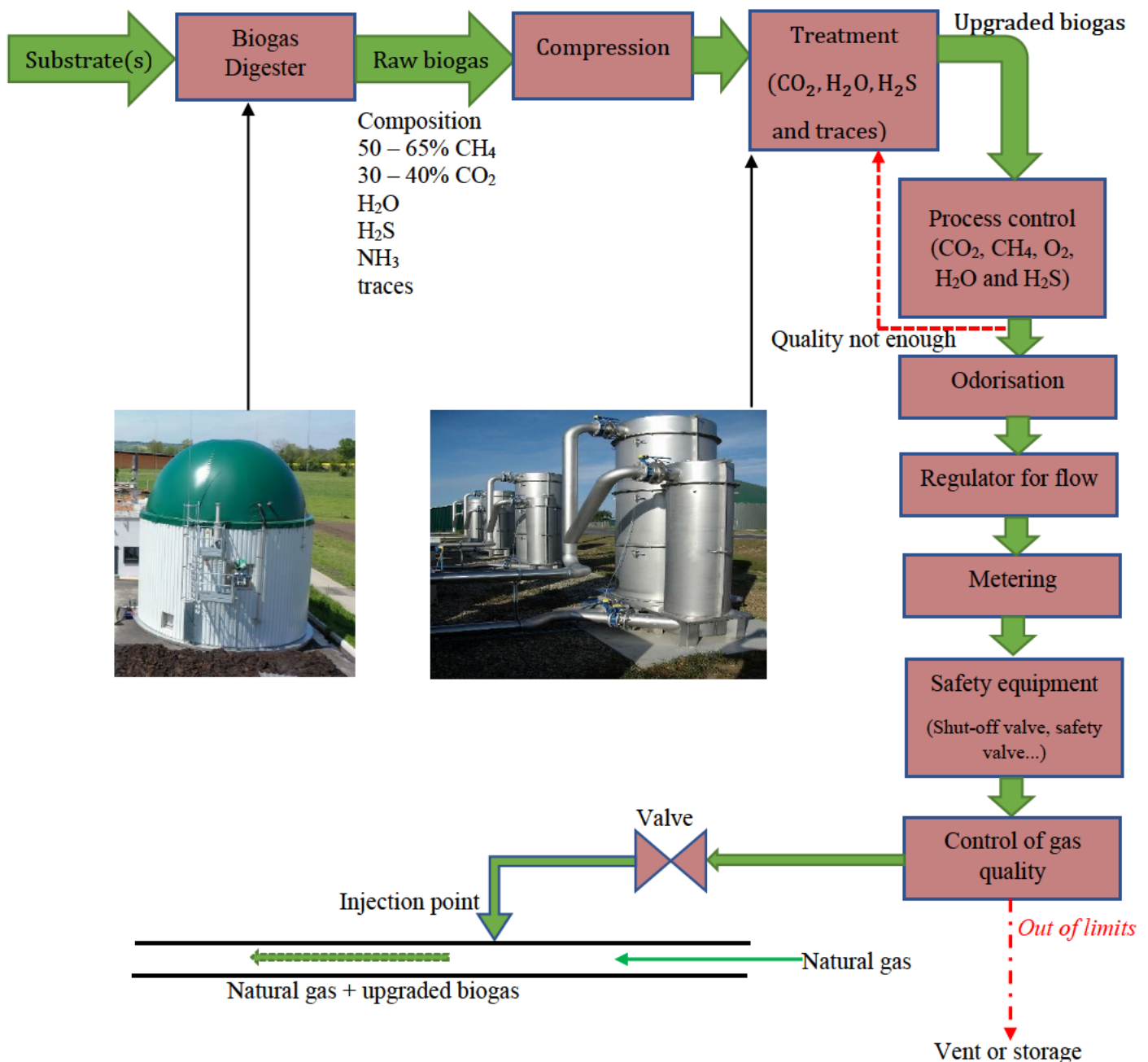
involve removing harmful trace components, are relatively cheaper than upgrading processes, which are more expensive and involve removing inert gases such as carbon dioxide to purify the gas and increase the energy density. This can cause economic and technical problems for companies looking to introduce biogas into the grid. The balance between upgrading costs and market value for the gas must be considered, as upgrading can be costly, especially due to the CO₂ removal process. Therefore, cleaning and upgrading must be cost-competitive to maintain biogas advantages.

Various biogas upgrading technologies, such as PSA, water scrubbing, physical scrubbing, amine scrubber, membrane separation, and cryogenic, produce biomethane meeting local standards for grid injection or vehicle fuel. However, these technologies require 0.2 to 0.75 heat (272) and 0.1 to 0.6 kWh/Nm³ electricity (273–275), with output biomethane purity ranging from 83% to 99.5% (276,277).

This work aims to explore opportunities to reduce the electrical and thermal energy demand for the biogas upgrading. In the proposed approach, the MCFC with its Balance-of Plant (BoP) functions as CO₂ separator. This approach has been conceptually proven in literature where the MCFC has shown promising result for CO₂ removal in several case studies. Amorelli et al. (278) investigated the use of MCFC for CO₂ removal from gas turbine exhaust gases, achieving up to 50% removal. Lusardi et al. (279) studied fuel cell systems for CO₂ separation from thermal plant exhaust, finding that emissions could be reduced below the Kyoto Protocol limit without separation or by 68% with a separator. Another study revealed up to 80% CO₂ removal using MCFC in cryogenic separation, with a 22% increase in power usage and 59% efficiency (184). Energy demand for current biogas upgrading technologies is high, potentially hindering the shift towards biogas usage due to the trade-off between upgrading costs and market value. This study presents a new concept of coupling a MCFC with a SOE for biogas upgrading to

biomethane with minimal or zero energy requirements. The goal is to demonstrate an effective and energy-efficient decarbonisation process, evaluated through system-level simulations across various operating scenarios.

Figure 6.1: Diagram of the process for injecting biogas into the natural gas network [3]



6.2 The proposed process description

Water and treated biogas, i.e., devoid of impurities like H₂S, halogenated compounds, and H₂O, are supplied to the cathode of the SOE and MCFC, respectively, as depicted in **Figure 6.1**. The SOE produces pure hydrogen at its cathode, which is subsequently introduced into the MCFC's anode. Concurrently, the SOE anode produces a pure oxygen stream directed to the MCFC cathode, where CO₂ is captured and transferred to the anode, as illustrated in **Figure 6.1**.

The primary concern of the proposed process, which may first occur to the reader, lies in the possible side reactions that may occur in the cathode of the MCFC due to it being fed with a mixture containing CO₂, CH₄, and O₂. Equations (6.1) - (6.3) show the list of possible reactions along with their respective reaction conditions, which include partial oxidation of methane, combustion of methane, and dry reforming of methane.

Reaction Equation	Name of Reaction	Reaction conditions	
$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	Partial Oxidation of Methane	1127°C, 50 - 70 bar (280–282), 700°C and 900°C, 1 bar with catalyst (283–285)	(6.1)
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	Combustion of Methane	600°C (286)	(6.2)
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	Dry Reforming of Methane	700 to 950°C with catalyst (287)	(6.3)

As can be observed, all the concerning side reactions occur at temperatures above 600°C. Consequently, the MCFC operating temperature is maintained at 575°C. Furthermore, the most studied metal catalyst for these reactions has been nickel (Ni) due to its high activity and low cost (288), which is one of the materials used for the MCFC cathode electrode. Nevertheless, this can be replaced with a lithium compound such as lithium metatitanate (289–291) in order to lower the chance of the aforementioned side reactions.

The methane-rich effluent from the MCFC cathode will first undergo cooling through a heat exchanger, supplying the district heating network with hot water at 80°C. It is then directed to a membrane-based technology for O₂ removal, before being fed to storage or injected into the natural gas grid. The MCFC anode effluent is first directed to a post-combustion chamber to completely burn the unreacted H₂ in pure O₂, forming H₂O. This is then cooled through a heat exchanger, supplying additional hot water at 80°C to the district heating network. The cooled effluent is passed through a condenser to condense the H₂O, which is then removed. The exhaust, predominantly CO₂, can be compressed and liquefied. The liquefied CO₂ can be bottled and sold to industries for various chemical processes.

In this work, the system performance analysis and optimisation will focus on CO₂ removal energy requirements to investigate effectiveness of the proposed process in contrast to the existing processes. Moreover, process sensitivity analysis tools for primary operating parameters such as oxidant composition and fuel utilisation were deployed to capture and evaluate the behaviour of the proposed system for various scenarios.

6.3 Simulations overview

Two main subsystems, SOE and MCFC, previously developed using Aspen Plus[™] in our studies, were integrated to simulate the Balance of Plant (BoP) depicted in **Figure 6.2**. Each subsystem features its own flowsheet and auxiliary units. Modelling, simulation, and validation of individual subsystems were conducted in our previous studies (Chapter 4 and Chapter 5, respectively), while the integration of subsystem simulators to compute mutual interactions and capture interfacing data was executed in the current study. This coupling allows for the evaluation of the entire plant's mass and energy balances, providing insight into the system's overall energy demand.

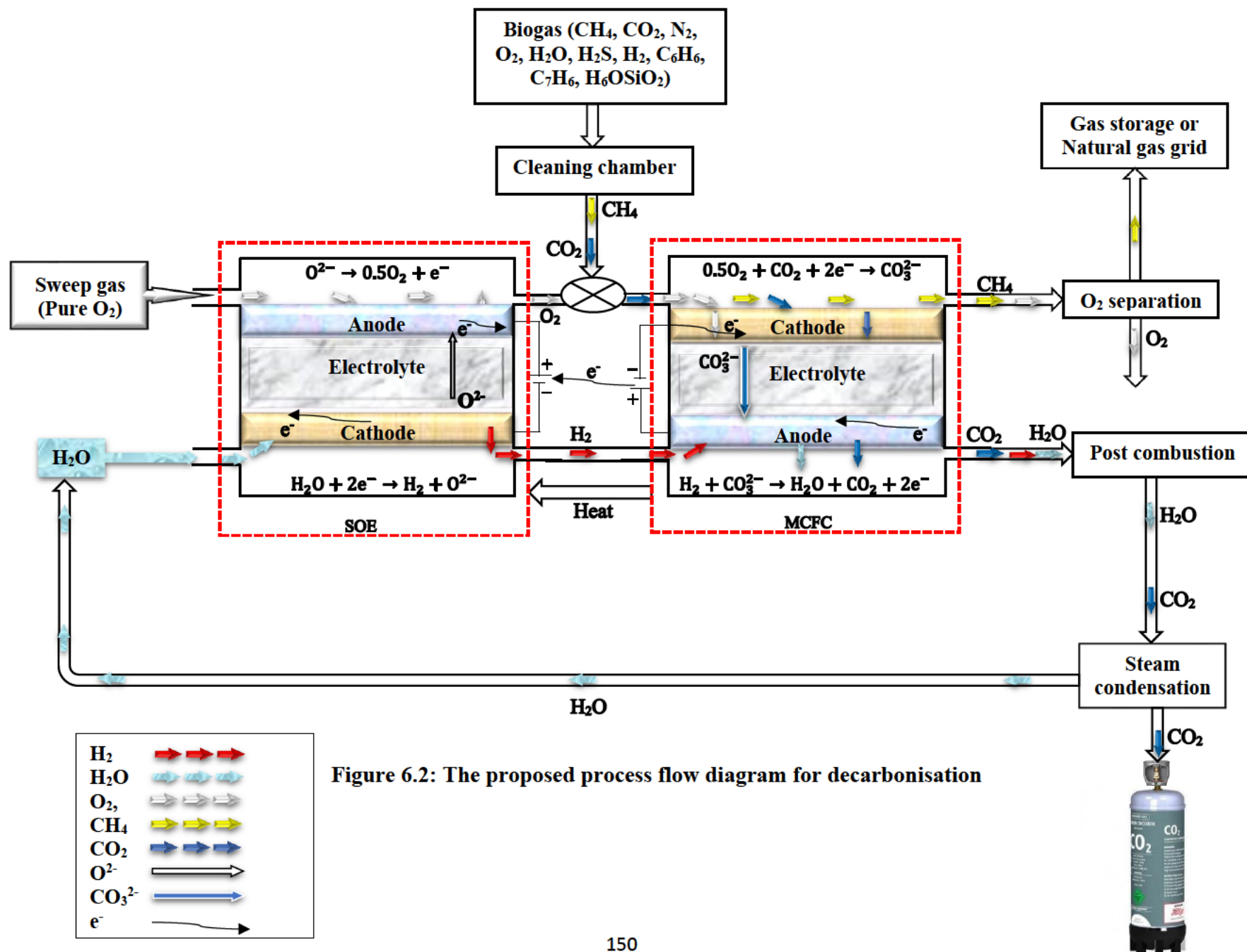


Figure 6.2: The proposed process flow diagram for decarbonisation

Understanding system behaviour is facilitated by the former data, while the latter is essential for determining the proposed system's energy self-sufficiency. Effective integration of the two subsystem units for optimal heat recovery in each plant unit is crucial for achieving high overall plant efficiencies. The proposed integration is expected to enhance MCFC and SOE conversion efficiency, positively influencing the plant's energy balance. This configuration may necessitate the removal or addition of certain components relative to the individual subsystem simulations presented in our previous studies (Chapter 4 and Chapter 5). Further details will be elaborated in the proceeding section.

6.4 Model flowsheet

The MCFC and SOE were simulated using a zero-dimensional model, which estimates their thermodynamic properties, energy balances, and gas compositions at the cathode and anode outlets for both the fuel cell and electrolyser based on the reactants' device utilisation factors (i.e., fuel, oxidant, and steam utilisation factor respectively) and feed compositions. **Figure 6.3** presents the integrated model flowsheet for the two subsystem units. In the SOE section, the steam generator unit, denoted as 'BOILER', has been replaced with a heat exchanger, transitioning from its initial role as a heater in the previous model. The heat exchanger's HOT-IN stream, designated as 'MS1', now receives the hot exhaust from the MCFC anode. This modification eliminates the requirement for external energy input for steam generation. The hot exit stream from the SOE anode (An-out), designated 'O₂', primarily composed of oxygen, serves to preheat the fresh oxygen stream ('O₂') sourced from oxygen storage tank via heat exchanger 'HE-3'. The resulting exit stream, 'O₂-S3', retaining residual thermal energy, preheats incoming raw biogas within heat exchanger 'HE-4'. Subsequently, the preheated biogas combines with oxygen in the 'MIXER' block, forming the stream 'MCATH-IN', which is introduced into the MCFC cathode inlet ('M-CATHODE'). 'O₂-S4', the exit stream from 'HE-4', is directed to the oxygen storage tank, later supplying the SOE as sweep gas and the MCFC

as oxidant. The upgraded biogas, designated as 'Biomethane', exits the MCFC cathode and is directed to natural gas storage or the natural gas grid.

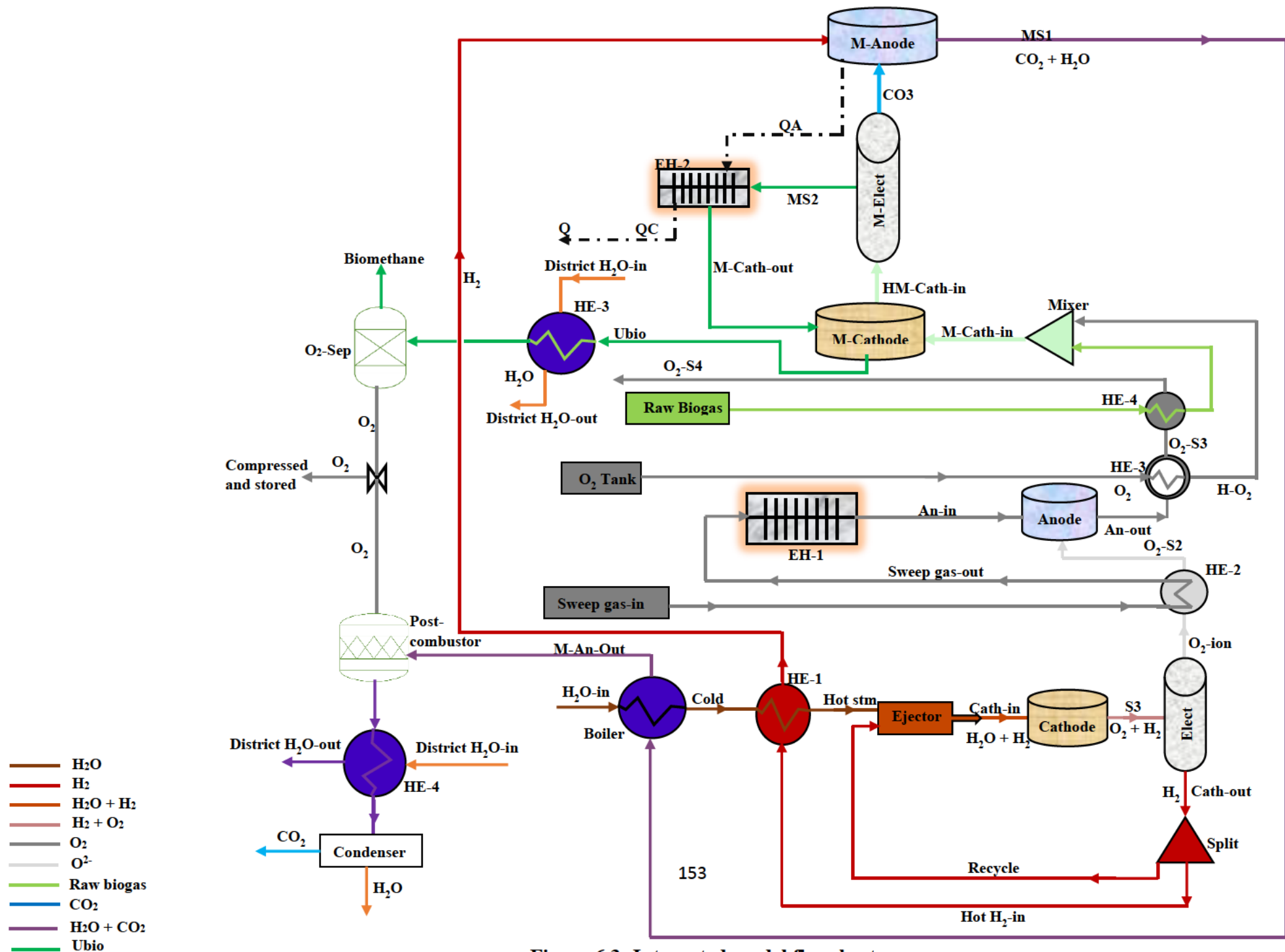


Figure 6.3: Integrated model flowsheet

The SOE anode exit stream, denoted as 'H₂', predominantly contains hydrogen gas and a minor proportion of steam at elevated temperatures, which is directly channelled to the MCFC anode inlet, thus obviating the need for fuel preheating. Detailed explanations of the model simulations for both subsystems, not addressed in this study, are available in our previous studies (Chapter 4 and Chapter 5).

The facile thermal integration demonstrated in the proposed process suggests it as a promising alternative approach for conventional, energy-intensive decarbonisation processes and the production of high-quality biomethane.

6.5 Decarbonisation study

The primary aim of this work is to explore the effectiveness of the proposed system for biogas upgrading and decarbonisation. It explores the biogas upgrading capabilities of the proposed integrated SOE-MCFC system using two types of biogases of different composition, labelled (BG-1) and (BG-2) (see **Table 6.2**). The decarbonisation process of flue gas was also assessed with the proposed integrated system, using two types of flue gas of different composition, namely Flue gas type 1 (FG-1) and Flue gas type 2 (FG-2) (Table 2). The SOE and MCFC input parameters applied for this decarbonisation simulation are provided in **Table 6.1** and **Table 6.2**, respectively.

Table 6.1: SOE input parameters

Type	Value
H ₂ O feed	1 kmol/hr
H ₂ O feed Temperature	25 °C
H ₂ O feed Pressure	1.013 bar
Steam Concentration in SOE cathode	90%
SOE operating temperature	800 °C
SOE Operating Pressure	1.013 bar
Sweep gas type	pure O ₂
Steam Utilisation factor	85%
Molar flow rate ratio of sweep gas to H ₂ O feed	1
Total active area	20 m ²

Table 6.2: MCFC input parameters

Type	Value
Biogas-1 Composition (BG-1)	CO ₂ 50%, CH ₄ 50%
Biogas-2 Composition (BG-2)	CO ₂ 38%, CH ₄ 60%, N ₂ 1%, and O ₂ 1%
Flue gas-1 Composition	CO ₂ 7%, H ₂ O 15%, N ₂ 75%, and O ₂ 3%
Flue gas-2 Composition	CO ₂ 15%, H ₂ O 15%, N ₂ 65%, and O ₂ 5%
Raw Biogas feed and flue gas Temp	26 °C
Raw Biogas feed and flue gas Pressure	1.013 bar
Fuel utilisation factor (U _f)	85 %
MCFC operating temp	575 °C
MCFC Operating Pressure	1.013 bar
Total active area	100 cm ²

6.5.1 Gas upgrading performance.

This section investigates the impact of the CO₂ fraction in the raw biogas on the net power output of the integrated SOE-MCFC system defined in the Equation (6.4) - (6.6).

$$\text{Net Power Output} = \text{MCFC}_{P_T} - \text{SOE}_{P_T} \quad (6.4)$$

$$\text{MCFC}_{P_T} = \text{MCFC}_{P_{\text{Elect}}} + \text{MCFC}_{Q_{\text{Th}}} \quad (6.5)$$

$$\text{SOE}_{P_T} = \text{SOE}_{P_{\text{Elect}}} + \text{SOE}_{Q_{\text{Th}}} \quad (6.6)$$

Where $\text{SOE}_{P_{\text{Elect}}}$ is the electrical power required by the SOE, $\text{SOE}_{Q_{\text{Th}}}$ is the thermal power required by the SOE, SOE_{P_T} is the total power required by the SOE, $\text{MCFC}_{P_{\text{Elect}}}$ is the electrical power generated by the MCFC, $\text{MCFC}_{Q_{\text{Th}}}$ is the thermal power generated by the MCFC and MCFC_{P_T} is the total power generated by the MCFC. As depicted in **Figure 6.4**, with the MCFC's fuel utilisation factor set at 0.85, a distinct cubic relationship is observed between the BG-1 CO₂ fraction and the system's net thermal power output as the BG-1 CO₂ fraction increases from 0.2 to 0.6. This trend can be attributed to the exothermic electrochemical reactions occurring within the MCFC. Specifically, the MCFC exploits the reaction of CO₃²⁻ with H₂ (derived from the SOE) to generate electricity and heat. The net thermal power output demonstrates a substantial increase from 0.004 kWh/Nm³ to 0.331 kWh/Nm³. As the BG-1

CO₂ fraction increases, more CO₂ becomes available to engage in the electrochemical reactions, effectively increasing the reaction rate and raising the cathode exit temperature as illustrated in **Figure 6.5**, thereby increasing the system's net thermal power output.

Conversely, the biomethane volumetric flow rate, as depicted in **Figure 6.5**, displays a decreasing trend as the BG-1 CO₂ fraction increases. A conceivable explanation for this behaviour lies in the reaction stoichiometry within the MCFC. An increased CO₂ fraction implies a greater availability of CO₂ for reactions, which reduces the inflow of raw biogas required and subsequently decreases the biomethane volumetric flow rate. This reduction in biomethane flow rate also contributes to the enhanced system's net thermal power output, as less heat is dissipated with the outflow of biomethane.

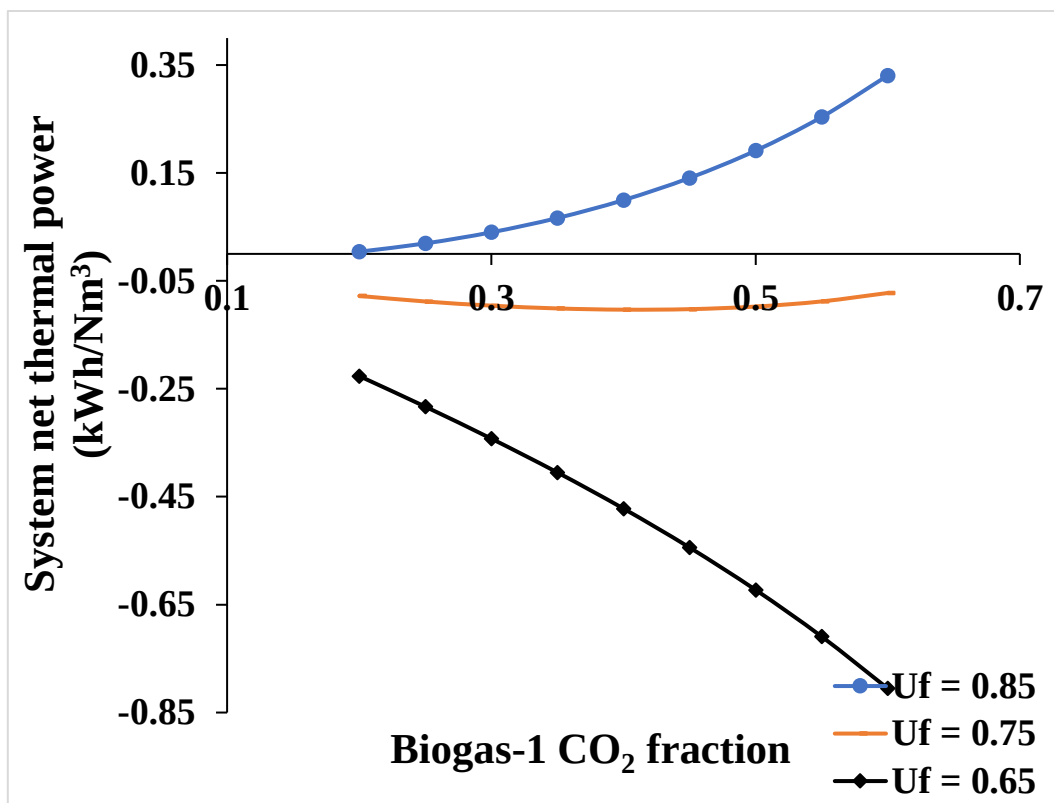


Figure 6.4: Effect of BG-1 CO₂ fraction on the system's net thermal power at different MCFC fuel utilisation factor

In contrast, for the MCFC's fuel utilisation factors of 0.75 and 0.65, the integrated SOE-MCFC system not only fails to generate a net thermal power output, but it also requires both external

electrical and thermal power inputs for the decarbonisation process of raw biogas into biomethane, as indicated by the negative results observed in **Figure 6.4**. A parabolic relationship is observed between the BG-1 CO₂ fraction and the system's total power input as the BG-1 CO₂ fraction varies from 0.2 to 0.6 for the fuel utilisation factor of 0.75, with the peak total power input of 0.1 kWh/Nm³ occurring at a BG-1 CO₂ fraction of 0.4. Similarly, a visibly cubic increase is evident in the total power input for the MCFC's fuel utilisation factor of 0.65, ranging from 0.226 kWh/Nm³ to 0.805 kWh/Nm³ as the BG-1 CO₂ fraction is varied from 0.2 to 0.6. This observation can be attributed to the fact that the fraction of unconverted fuel gas (H₂) produced by the SOE increases as the MCFC's fuel utilisation factor decreases, resulting in energy losses (both electrical and thermal) within the integrated SOE-MCFC system. This necessitates an external total power input of the magnitude depicted in **Figure 6.4**, contingent on the fuel utilisation factor and the biogas CO₂ fraction for the decarbonisation process of the raw biogas into biomethane. The previously established reasoning for biomethane volumetric flow rate and cathode temperature for a fuel utilisation factor of 0.85 also applies for MCFC's fuel utilisation factors of 0.75 and 0.65.

It can be concluded that to make the current proposed process viable in the biomethane production industry, the MCFC must be maintained at a fuel utilisation factor of 0.85 to compete with existing biomethane production technologies in terms of energy consumption. The model is deployed to compare the proposed system performance compared to existing carbon removal technologies.

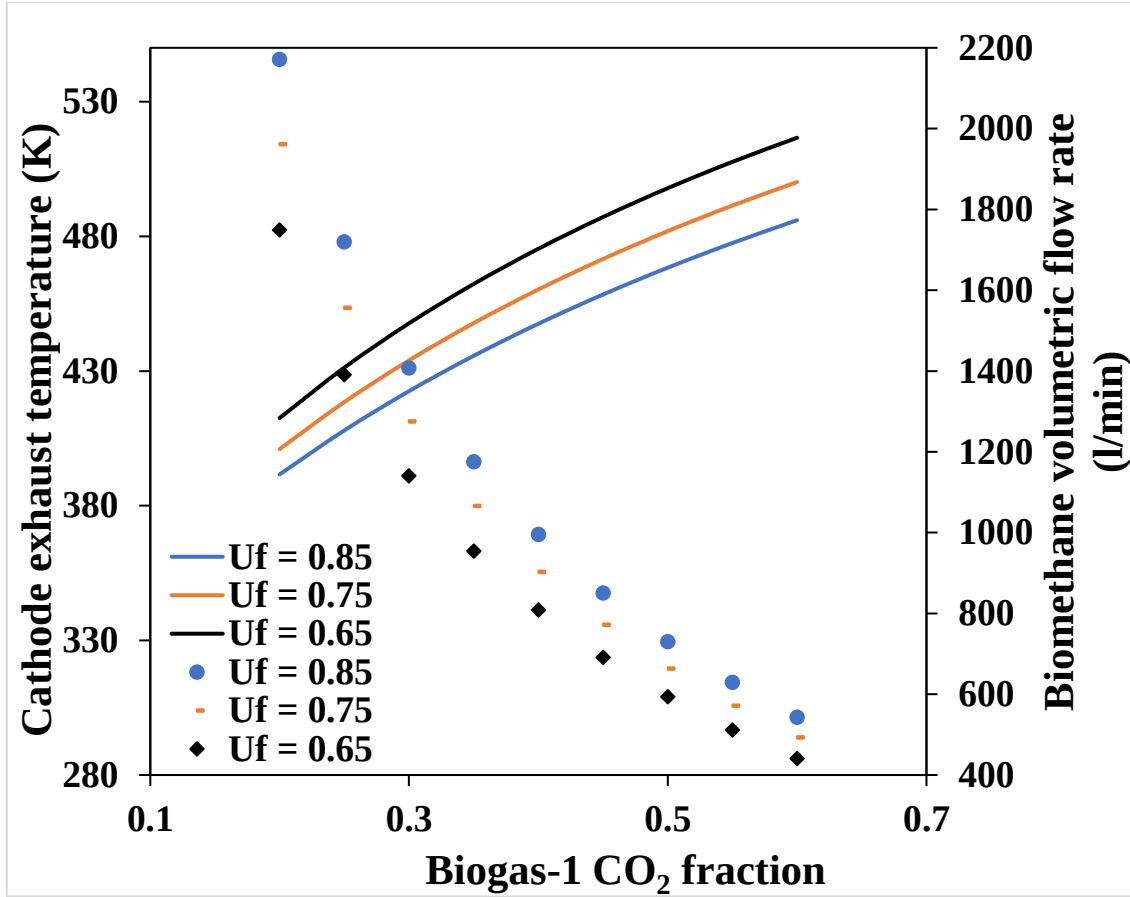


Figure 6.5: Effect of BG-1 CO₂ fraction on the cathode exit stream temperature (line graph) and Biomethane volumetric flow rate (dotted graph)

6.5.2 Performance Evaluation of the Decarbonisation Process

Table 6.3 presents the performance assessment of the system. The proposed methodology achieved a CO₂ capture efficiency of 87.5% for both BG-1 and BG-2, yielding net thermal power outputs of 4.9 and 3.8 kW_{th}, respectively. The SOE, requiring 54.4 kW of electrical and 22.7 kW of thermal power, generates a fuel composition of 86.5% H₂ and 13.5% H₂O via the electrolysis of water at 25°C (refer to Table 6.1), culminating in an energy efficiency of 85.35%. Upon integration, as depicted in Figure 6.2, the MCFC generates electrical and thermal power outputs of 33.22 kW and 48.75 kW respectively, achieving an electrical conversion efficiency of 50.49%.

The overall integrated system releases a net thermal power output of 4.89 kW for BG-1. Conversely, for BG-2, the MCFC generates electrical and thermal power outputs of 32.44 kW

and 48.40 kW respectively, achieving an electrical conversion efficiency of 49.31%. The overall integrated system results in a net thermal power output of 3.76 kW. The observed discrepancy in the system's performance improvement for BG-1 is attributable to its enriched CO₂ content relative to BG-2, as discussed in the preceding section. This finding aligns with our previous study (Chapter 5), where it was established that the MCFC demonstrates enhanced performance in terms of electrical and thermal energy generation when pure CO₂ and O₂ are used as the oxidant. Evidently, due to the same underlying factors, the overall integrated system's net thermal power for flue gas-1 is the least among those investigated in the present study, with a value of 0.73 kW. The CO₂ capture rate for all the investigated CO₂ source oxidants is 37.40 kg/hr. This rate appears to remain constant despite variations in the CO₂ source oxidant. This can be attributed to the fact that the hydrogen production from the SOE is unaffected by changes in the CO₂ source oxidant of the MCFC. As a result, the same amount of CO₂ is required to form sufficient carbonate ions for hydrogen oxidation at the MCFC anode.

Table 6.3: Overall system output for decarbonisation Process

Outputs	BG-1	BG-2	Flue gas-1	Flue gas-2
Cell voltage (V)	0.729	0.712	0.678	0.737
MCFC electric power released (kW)	33.22	32.44	30.90	33.59
MCFC thermal energy released (kW)	48.75	48.40	46.91	46.92
MCFC electric efficiency (%)	50.49	49.31	46.97	51.06
CO ₂ removal efficiency (%)	87.50	87.50	54.00	25.80
SOE electric power required (kW)	54.40	54.40	54.40	54.40
SOE thermal energy required (kW)	22.68	22.68	22.68	22.68
SOE energy efficiency (%)	85.35	85.35	85.35	85.35
System net thermal power (kW)	4.888	3.758	0.728	3.432
Biomethane production rate (kg/hr)	20.93	30.67		
CO ₂ captured (kg/hr)	37.40	37.40	37.40	37.40
Hot water at 80°C for district heating (kg/s)	0.067			

The biomethane production yields for BG-1 and BG-2 stand at 20.93 kg/hr and 30.67 kg/hr respectively, while the methane fractions, indicative of the biomethane's purity, are 88.89% and 91.26% respectively, as outlined in **Table 6.4**.

Table 6.4: Comparison between the composition of the raw and upgraded biogas.

Component	Raw BG-1 (%)	Upgraded BG-1 (%)	Raw BG-2 (%)	Upgraded BG-2 (%)
H ₂	0.000	0.000	0.000	0.000
O ₂	0.000	0.000	1.000	0.000
CO ₂	50.00	11.11	38.00	7.224
CH ₄	50.00	88.89	60.00	91.26
N ₂	0.000	0.000	1.000	1.519

These outcomes are intrinsically linked to the quality of the raw biogases; the superior quality of BG-2 facilitates a higher-grade biomethane and an increased production rate due to its lower initial CO₂ content. A higher flow rate is thus necessitated to supply the CO₂ required for the formation of carbonate ions, integral to hydrogen oxidation in the MCFC anode. The detailed stream data for upgrading BG-1 is shown in **Table 6.6**.

Intriguingly, despite BG-2 facilitating superior biomethane production and purity, it results in a lower system net thermal power compared to BG-1. A trade-off will inevitably emerge in real-world implementations of this technology, necessitating a balance between the quality of the raw biogas or the available raw biogas, and the system's power output. Process engineers will need to make strategic decisions based on stakeholder priorities, striking a balance between net power output and the purity and production rate of biomethane.

Table 6.5: Performance Comparison of different commercial biogas upgrading technologies against the present study (268)

Technologies	Electricity Consumption (kWh/Nm ³)	Heat energy consumption (kWh/Nm ³)	% Purity
PSA	0.3 – 1	-	83 – 99
Water Scrubbing	0.3 - 0.6	-	97
Physical Scrubbing	0.4	< 0.2	93 - 97
Amine Scrubber	0.12	0.75	97.5 - 99.5
Membrane separation	0.14	-	90 – 98
Cryogenic	0.67	-	98
Present study	-0.19* (The system generated net thermal power)		> 85

*Raw biogas composition – BG-1 (50% CH₄ and 50% CO₂)

Table 6.5 provides a comparative analysis of the proposed technology with extant methodologies in the market, with a particular emphasis on energy consumption metrics. Our technology advances over traditional approaches as it negates the necessity for external electricity or thermal energy demand, instead producing a net system thermal power of 0.19 kWh/Nm³ of biomethane by upgrading BG-1. The system's net thermal power, ranging between 3.70 - 4.9 kW based on the quality of raw biogas utilised (as shown in **Table 6.3**), presents an opportunity for further research to convert this thermal power into electrical energy via a steam turbine, thereby generating surplus electricity for potential injection into the national grid.

Thus, the comparison inherently favours the solution presented in this study, as the operational energy cost could potentially be nullified, or even reversed, to generate surplus energy that can be fed into the national grid. However, contrary to this, is the consideration of costs and the inherent complexity of the plant design. Presently, the installation costs for standalone MCFC and SOE plants are approximately 2372 £/kWe (292) and 381 £/kWe (293) respectively, which may not present an economically attractive proposition unless the investment cost can be amortised over a twenty-year operation period. Nonetheless, if future advancements lead to a

reduction in the cost of SOE and MCFC plants, solutions such as the one proposed in this paper could prove to be highly cost-effective.

Table 6.6: Detailed stream data obtained from the model simulation operating condition using BG-1 as shown Figure 6.2

Stream Name	Temperature	Pressure	Mole	Mole Fractions				
	°C	bar	Flows kmol/hr	H ₂	O ₂	CH ₄	CO ₂	H ₂ O
H ₂ O-in	25	1.013	1.000	-	-	-	-	1.000
Cold Stm	101.5	1.013	1.000	-	-	-	-	1.000
Hot Stm	334.5	1.013	1.000	-	-	-	-	1.000
Recycle	800.0	1.013	0.131	0.865	-	-	-	0.135
Cath-in	380.8	1.013	1.131	0.100	-	-	-	0.900
S3	800.0	1.013	1.563	0.626	0.277	-	-	0.098
Cath-out	800.0	1.013	1.131	0.865	-	-	-	0.135
Hot H ₂ -in	800.0	1.013	1.000	0.865	-	-	-	0.135
O ₂ -S2	800.0	1.013	0.433	-	1.000	-	-	-
Sweep gas-in	25.00	1.013	1.000	-	1.000	-	-	-
An-in	800.0	1.013	1.000	-	1.000	-	-	-
An-out	502.5	1.013	1.433	-	1.000	-	-	-
O ₂ -S3	390.4	1.013	1.433	-	1.000	-	-	-
O ₂ -S4	161.4	1.013	1.433	-	1.000	-	-	-
H ₂	344.5	1.013	1.000	0.865	-	-	-	0.135
O ₂ Tank	25.00	1.013	0.472	-	1.000	-	-	-
H-O ₂	389.4	1.013	0.472	-	1.000	-	-	-
Raw Biogas	26.00	1.013	1.943	-	0.000	0.500	0.500	-
H-RBio	160.4	1.013	1.943	-	-	0.500	0.500	-
M-Cath-in	194.9	1.013	2.415	-	0.196	0.402	0.402	-
HM-Cath-in	453.5	1.013	2.415	-	0.196	0.402	0.402	-
MS2	453.5	1.013	1.140	-	0.041	0.852	0.107	-
M-Cath-out	575.0	1.013	1.140	-	0.041	0.852	0.107	-
Ubio	195.4	1.013	1.140	-	0.041	0.852	0.107	-
CO3	453.5	1.013	1.275	-	0.333	-	0.667	-
MS1	575.0	1.013	1.850	0.008	-	-	0.459	0.532
M-An-out	102.5	1.013	1.850	0.008	-	-	0.459	0.532
CO ₂	26.46	1.013	0.851	-	-	-	1.000	-
Biomethane	48.27	1.013	1.0928	-	-	0.8889	0.1111	-
O ₂	48.27	1.013	0.047	-	1	-	-	-

6.6 Significance of the present study in power-to-gas (PTG)

The current study holds substantial relevance for the PTG industry, especially considering the dynamics of the transforming energy sector. As the global energy paradigm shift towards environmentally sustainable solutions, the strategic integration of renewable energy resources

to harness surplus energy during peak production periods becomes of paramount significance. The PTG technology is based on the Sabatier reaction (i.e., synthesis of natural gas via CO_2 and H_2), which involves the conversion of electrical energy into a gaseous fuel, emerges as a promising innovation. It facilitates energy storage solutions and acts as a critical link in interconnecting the electrical and gas grid systems. The primary objective is to usher this technology towards commercialisation, thereby establishing it as a financially viable strategy for electrical energy storage. This study offers profound understanding for the optimisation of PTG systems, specifically those involving the coupling of SOEs and MCFCs. In this framework, the MCFC is utilised to separate CO_2 from raw biogas, offering an innovative approach as opposed to the conventionally employed amine plants. Contrastingly, the SOE is deployed as an alternative to the alkaline electrolyser, thereby augmenting the efficiency of H_2 production and facilitating effective thermal and electrical synergies with the MCFC. The fundamental significance of this study to PTG industry resides in the proposed solution which harnesses CO_2 from raw biogas and converts it into methane via a highly exothermic reaction with hydrogen sourced from water electrolysis. This process would strategically utilise surplus or economically viable renewable electricity from the grid.

The proposed methodology offers potential for real-world application within existing industrial frameworks. The Synthesised Natural Gas (SNG) and the resultant upgraded biogas can be delivered to end-users through the pre-existing natural gas infrastructure, capitalising on its built-in storage capabilities. This system is capable of achieving a high degree of CO_2 capture efficiency, delivering CO_2 to the methanator at the optimal temperature range of 200–400 °C. This negates the need for external thermal energy input for process heating, whilst concurrently generating a net thermal power output. Beyond the technical aspects, economic considerations are of significant importance. The increased operational temperature presents a substantial advantage. Both proposed modifications are rooted in high-temperature electrochemical

processes. These elevated temperatures markedly increase all chemical reactions, thereby eliminating the need for costly catalysts such as platinum. The construction of both MCFC and SOE incorporates nickel-based electrodes, which further enhances their cost-effectiveness. This represents a notable departure from existing PTG technologies that typically consume external electricity or thermal energy for CO₂ capture. The study further explores the potential for surplus energy generation within the proposed system. The net thermal power output, as demonstrated in this study, could be converted into electricity via a steam turbine, thereby producing additional electricity that could contribute to the national grid. The ability to design a self-sustaining system that not only contributes to CO₂ capture and biogas upgrading but also generates excess energy represents a significant leap forward in PTG technology.

CHAPTER 7: MODELLING AND SIMULATION OF A SOLID OXIDE FUEL CELL

7.1 Introduction

Solid oxide fuel cells (SOFCs) are high temperature (i.e. 500 to 900 °C) fuel-to-power devices (65) which accept directly not only hydrogen, but also hydrocarbons (66) such as CH_4 , $\text{C}_2\text{H}_5\text{OH}$ (67), C_3H_8 (68,69), or reformed $\text{CO}(\text{NH}_2)_2$ (70) as fuel for generation of power through electrochemical reactions. Syngas (CO , H_2) from various biomass gasification processes and ammonia (NH_3) are also potential fuels. The fuel to power conversion in SOFC is mostly characterised by high electrical efficiency as compared to internal combustion engines (ICEs).

Solid oxide fuel cells and other high temperature fuel cells processes the advantage of co-generation application. The development of a fuel cell (FC) system requires more than the consideration of an optimised system in terms of its energy efficiency and cost effectiveness, but also entails the study of the balance of plant (BoP) considering that the BoP will directly affect overall plant efficiency, which could negatively impact the cost effectiveness of the fuel cell system.

Several investigations (294) have been carried out on solid oxide fuel cell model development, particularly, the tubular configuration (295–297) but all of which are time-consuming in computations and are not easily integrated in the fast-moving technological developments observed in the research area. As was executed for the MCFC in Chapter 5, a system-level simulation model of the SOFC stack was also developed in AspenPlus™, serving as a component in the decarbonisation and power-to-gas integrated plant project. This development relied on system-level features and first-principle models, providing intricate insights into the

mass/charge transport, thermodynamics, and heat transfer of the SOFC system, thereby serving as a guide for SOFC operation. The simulation model underwent validation against published data and was subjected to a sensitivity analysis of key parameters in SOFC operations, including current density, fuel utilisation factor, and steam to carbon ratio.

In this study, the available unit modules and functions in AspenPlus™ proposed by (257) were employed for the development of the SOFC stack model with the least need for subroutine linkage. The strategy applied here; provide a means to wholly employ the available capabilities, i.e., the equilibrium model, which is built on the phenomenon of Gibbs free energy minimisation, thus offering an easy means to study the parametric sensitivity and thermodynamic analysis of the overall fuel cell plant. The voltage calculation employed in this study considers losses from concentration limitations (298), activation energy (299) and ohmic resistance (300).

7.2 Solid Oxide Fuel Cell operation

The fundamental structure of an SOFC is composed of a solid electrolyte, typically a ceramic material, sandwiched between an anode and a cathode (301), as illustrated in **Figure 7.1**. hydrogen gas, a fuel derived from hydrocarbon (in this case, methane) through steam reforming as illustrated in Equation (7.1) and (7.2), is supplied to the anode electrode, and oxidant (air or pure oxygen) is introduced at the cathode electrode. The oxygen in the oxidant stream undergoes an electrochemical reduction at the cathode electrode surface to generate oxygen ions (O^{2-}) as shown in Equation (7.3). The electrolyte matrix enables the ionic pathway for the O^{2-} . The O^{2-} then migrate through the electrolyte to the fuel electrode (anode) where the hydrogen gas in the fuel reacts with the O^{2-} , producing steam as shown in Equation (7.4). For simplicity, both the cathode and anode reactions are combined into a single equation known as

the overall cell reaction, incorporating the DC electrical power and the generated heat energy as shown in Equation (7.5).

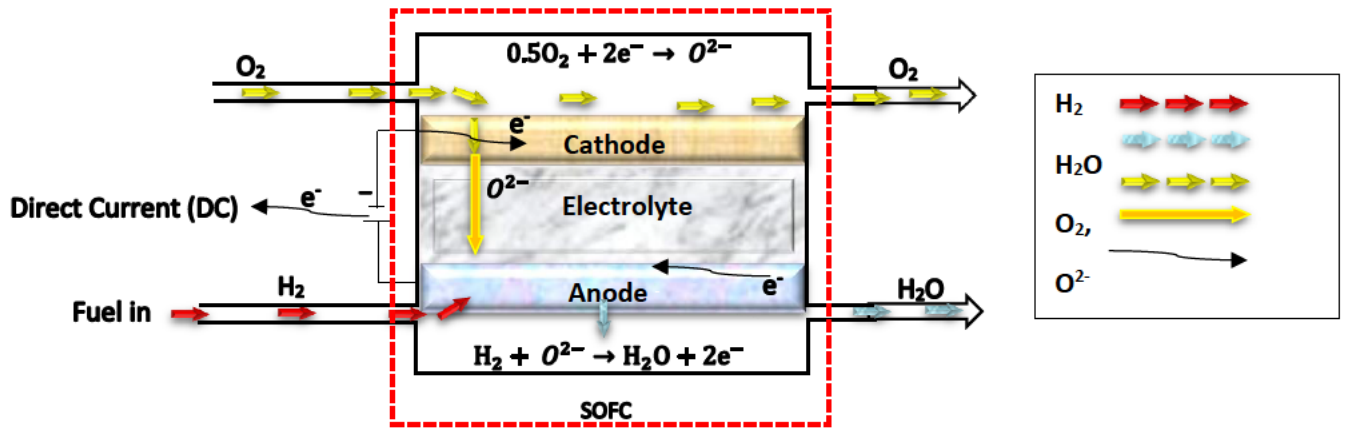


Figure 7.1: Fundamental operation of Solid Oxide Fuel Cell

Individual cells are connected in electrical series through a metallic interconnect to increase voltage and power, and they can be assembled to reach the desired stack size. Several stacks can be organised within a casing to construct an SOFC module. Single or multiple modules can be consolidated and coupled with subsystems to recuperate heat, and to convert the generated electricity from direct current (DC) to alternating current (AC), thereby building an SOFC power system.

7.3 Simulation Method

The objective of this study was to develop a detailed model of an SOFC, utilising the commercially available AspenPlus™ software, to ultimately explore the technical feasibility

of integrating the SOFC model with other sub-models developed for the power-to-gas energy system plant proposed in Chapter 1. The main objective was to estimate the electricity and thermal energy generated, and to determine the product component composition of both the anode and the cathode of the SOFC which serve as the feed input for other sub-models within the overall proposed power-to-gas energy system plant.

The Aspen PlusTM simulation package employed for the SOFC steady-state modelling in this study has been reported in several investigations for the modelling of fuel cell based power generation systems (251–256). The simulation begins with the development of the cell model of an SOFC. The calculator block of AspenPlusTM was used to interactively deliver the electrochemical computations needed for fuel cell modelling. The computation spreadsheet was configured based on the mass balance equilibrium for an SOFC, while cell voltage was determined using the Nernst equation to compute open circuit voltage (OCV). The model inputs include temperature, pressure, and anode and cathode side compositions and flow rates. Fuel cell operating parameters, such as pressure, temperature, cell area, and utilisation factors for fuel, and oxygen, are required as inputs. The outputs generated include current density, cell voltage, electrical power generated, and the composition of outlet flows.

7.3.1 SOFC model flowsheet

Figure 7.2 shows the Aspen Plus flowsheet of the SOFC stack. A concise description of the individual in-built models used in **Figure 7.2** is presented in **Table 7.1**. It shows the default IDs used in the AspenPlusTM models' library, ID deployed in this study, and a brief explanatory note of the individual unit.

Table 7.1: Individual in-built models in Aspen Plus™ used in the SOFC platform depicted in Figure 7.2

Default ID	Unit ID	Comment
Heater	AIRHEAT	Increase the temperature of the fresh air
	FUELHEAT	Increase the temperature of the fresh fuel
	COOLER	Adjust the temperature of the recycled fuel + fresh fuel mixture to the pre-set reformer temperature
	HEATER1	Heats the product stream of the post-combustion
	HEATER2	Heats the exhaust of the cathode to the anode exhaust temperature.
Sep	CATHODE	Delivers electrochemically required amount of Oxygen to the anode.
Mixer	EJECTOR	To model mixing of the recycle stream and fresh fuel
HeatX	HEATX	To model post-heating of the post-combustion exhaust stream
RGibbs	REFORMER	To model steam reforming reaction of hydrocarbons and or water gas shift reaction of carbon monoxide to hydrogen
	ANODE	To model the electrochemical reaction of H ₂ and O ₂
Rstoic	POSTCOMB	To model the complete combustion of the unreacted fuel with the remaining O ₂ in the air stream
Fsplit	SPLIT	To model the splitting of the anode exhaust stream

7.3.2 Simulation assumptions

The SOFC modelling employed in this study assumed the following theories

100 The model is zero-dimension.

101 The model ignores pressure drops across the unit operation blocks.

102 The reformer is assumed to undergo an adiabatic reaction.

103 The hydrogen oxidation reaction i.e., Equation (7.5) is considered instead of ion transport.

104 All reactions are considered to be in chemical equilibrium.

105The model always assumes water gas shift reaction of carbon monoxide to hydrogen
and steam reforming of methane to hydrogen, so only hydrogen is oxidised in the anode.

106All operations are assumed to be in steady state and isothermal.

107All the fluids employed in the model obey the ideal gas law (252,257,258).

7.3.3 Modelling and simulation of SOFC

As shown in **Figure 7.2**, the 'FUELFEED' stream, which contain the fresh fuel, is fed to the 'FUELHEAT' block, modelling preheating of the fresh fuel. The preheated fresh fuel is then passed to the 'EJECTOR' block, where mixing of the recycle stream (containing mainly steam and carbon dioxide with a certain percentage of unreacted reformed fuel i.e., hydrogen and carbon monoxide) and fresh fuel occurs. The recycling ratio is predetermined by the set steam-to-carbon ratio (S/C) required for the steam reforming reaction in the 'REFORMER' block. The process was simulated by the Aspen Plus Fsplit and Mixer in-built model as shown in **Table 7.1**. The fresh fuel temperature, pressure and composition were specified. The blocks 'REFORMER' and 'COOLER' simulate the process that occurs in pre-reformers where the Equation (7.1) and (7.2) were modelled to attain equilibrium at the pre-reformer temperature. The block 'COOLER' adjusts the temperature of the reformer by using the design specification block (DS-1) to vary its temperatures until the 'REFORMER' block achieves adiabatic condition.

The stream 'AN-IN' from the 'REFORMER' block is passed to the 'ANODE' block for further steam reforming of the residual methane, water gas shifting of carbon monoxide and oxidation of hydrogen as shown in Equation (7.1) and (7.2). Modelling of ion movement is not feasible in Aspen plus, hence, hydrogen oxidation reaction i.e., Equation (7.5) was employed in the simulation.

However, direct oxidation of methane and carbon monoxide is achievable in high temperature fuel cells like solid oxide fuel cells, but this study assumed the complete steam reforming reaction of methane with water gas shift reaction of carbon monoxide to hydrogen. Thus, only hydrogen undergoes oxidation reaction in the ‘ANODE’ block and the Equation (7.1), (7.2) and (7.5) were employed in the model at a desired operating temperature.

The temperature of the fresh air, namely ‘AIR-IN’, is increased by passing it through the ‘AIRHEAT’ block and its outlet stream, namely ‘C-AIR-IN’, is fed to the heat exchanger ‘HEATX’ block to further preheat the air by the hot post combustion product stream. The design specification block (DS-2) is used to adjust the molar flow rate of fresh air in order to achieve the air utilisation factor of 0.167 (253).

The heated air is then fed to the ‘CATHODE’ block, where the required oxygen ($nO_{2,required}$) for the hydrogen oxidation reaction is being separated out by employing the calculator block using Equation (7.6) - (7.9).

$$nH_{2,in} = nH_{2,fuelfeed} + 1(nCO_{fuelfeed}) + 4(nCH_{4,fuelfeed}) + \dots \quad (7.6)$$

$$U_f = \frac{nH_{2,spent}}{nH_{2,in}} \quad (7.7)$$

$$nO_{2,required} = \frac{1}{2}nH_{2,spent} \quad (7.8)$$

$$O_{2,factor} = \frac{nO_{2,required}}{nO_{2,in}} \quad (7.9)$$

Where, $nH_{2,in}$ represent the molar flow rate of hydrogen available for the oxidation reaction in the anode of the SOFC, $nH_{2,fuelfeed}$ denotes the molar flow rate of hydrogen available in the fuel feed, $1(nCO_{fuelfeed})$ is the molar flow rate of hydrogen equivalent to the hydrogen generated from the water-gas shift reaction of CO available in the fuel feed, $4(nCH_{4,fuelfeed})$ represent the molar flow rate of hydrogen equivalent to the hydrogen generated from the steam

reforming of CH_4 in the fuel feed. And so the rest of higher hydrocarbons available in the fuel feed, $nH_{2,spent}$ represents the molar flow rate of hydrogen consumed in the electrochemical oxidation reaction, U_f represents the fuel utilisation factor of the system, which typically takes the value of 85%, $nO_{2,required}$ represents the molar flow rate of oxygen required in the electrochemical oxidation reaction, $nO_{2,in}$ represent molar flow rate of oxygen available in incoming fresh air and $O_{2,factor}$ is a factor number equivalent to the air utilisation factor of the system.

The required oxygen namely, 'O2' is fed to the block 'ANODE'. However, the spent air namely 'CATH-OUT' has to be at the operation temperature of the system i.e. (910°C) which is derived from the heat generated by the electrochemical reaction in real plant/system. Nonetheless, it was modelled by directing heat stream namely '(Q5)' from block 'HEATER2', which is specified temperature is at (910°C) to block 'ANODE'. The spent fuel namely 'AN-OUT' is fed to the 'SPLIT' block where it is being split in to 'RECYCLE' stream sent back to 'EJECTOR' block and 'SPLIT2' stream sent to the 'POSTCOMB' stream for post combustion reaction modelled by using the Equation (7.5) and (7.10). The design specification block was used to set the split ratio in order to achieve a desired/required steam-to-carbon ration (S/C) typically, a value of 2.5 (302). The complete combustion of the spent fuel ('SPLIT2' stream) and the spent air ('AIR-CATH' stream) is simulated in the 'POSTCOMB' block. The generated heat from the post combustion reaction namely stream 'Q4' is used to increase the temperature of the post combustion product stream ('COMBOUT') through the 'HEATER1' block. Lastly, the hot post combustion product steam ('HOT-IN') is used in heat exchanger ('HEATX') as the hot stream influent where the temperature of the heat exchanger effluent namely, 'HOT-OUT' also referred to as the SOFC stack effluent could be assessed.



7.3.4 Cell Voltage Computation

The computation of cell voltage in the simulation of every fuel cell is the most important aspect. The approach opted for in this study is the universally accepted Nernst model as the base equation for the reversible Nernst cell voltage (V_{NST}) Equation (7.11) coupled with voltage loss models which include activation loss, concentration loss and ohmic loss.

$$V_{NST} = - \left[\frac{\Delta \bar{G}_f}{2F} \right] + \left[\frac{R \cdot T_{AV}}{2F} \right] \ln \left[\frac{P_{H_2} \cdot P_{O_2}^{(\frac{1}{2})}}{P_{H_2O}} \right] \quad (7.11)$$

Where $\Delta \bar{G}_f$ is the molar Gibbs free energy of formation of steam at one bar ($Jmol^{-1}$), 2 is the number of moles of electrons released per mole of hydrogen consumed, F is the Faraday constant i.e., $96485 Cmol^{-1}$, T_{AV} is the mean temperature of the inlet and outlet streams of the SOFC stack (k), R is the Ideal gas constant i.e. $8.314 Jmol^{-1}k^{-1}$ and P_i is the partial pressure of the specie i obtained by taking the mean values of both inlet and outlet streams.

7.3.4.1 Voltage loss models

- i. Activation loss: This is the voltage loss due to the activation energy that the reactant component needs to attain for the reaction to occur. This can be obtained by employing the Achenbach (1994) model presented in Equation (7.12) and (7.13) due to the tardy kinetic nature of the electrochemical reaction occurring at the electrodes.

$$R_{ACTV_AN} = \frac{1}{\left[\frac{2 \cdot F}{R \cdot T_{AN}} \right] \cdot \left[\frac{P_{H_2}}{P^0} \right]^m \cdot k_{AN} \cdot \exp\left[\frac{-E_{AN}}{R \cdot T_{AN}}\right]} \quad \text{Anode} \quad (7.12)$$

$$R_{ACTV_CATH} = \frac{1}{\left[\frac{4 \cdot F}{R \cdot T_{CATH}} \right] \cdot \left[\frac{P_{O_2}}{P^0} \right]^m \cdot k_{CATH} \cdot \exp\left[\frac{-E_{CATH}}{R \cdot T_{CATH}}\right]} \quad \text{Cathode} \quad (7.13)$$

$$V_{ACTV} = j \cdot R_{ACTV} \quad \text{Voltage activation loss} \quad (7.14)$$

Where $R_{ACTV_{AN}}$ denotes specific resistance that occurred at the anode (Ωm^2), $R_{ACTV_{CATH}}$ denotes specific resistance that occurred at the cathode (Ωm^2), k_{AN} denotes the pre-exponential factor for anode ($213 \times 10^6 Am^{-2}$) (258), k_{CATH} denotes the pre-exponential factor for cathode ($149 \times 10^6 Am^{-2}$) (258), T_{AN} & T_{CATH} denotes operating temperatures across both anode and the cathode, P^0 denotes the reference pressure (1 bar), m is the slope obtained from the effect of partial pressures (0.25) (258), E_{AN} denotes the activation energy to be overcome at the anode, ($110 \times 10^3 Jmol^{-1}$) (258), E_{CATH} denotes the activation energy to be overcome at the cathode, ($160 \times 10^3 Jmol^{-1}$) (258).

- ii. Concentration loss: This is the voltage loss due to the limitations caused by the mass transfer of ion through the poriferous electrodes. The Equation (7.15) and (7.16) deduced from Knudsen's, ordinary and Fick's law of diffusion were used to model the voltage concentration loss at the anode and cathode respectively (298). Effective diffusion coefficients were employed in order to take the two types of diffusion into consideration.

$$V_{Conc_AN} = - \left[\frac{R \cdot T_{AN}}{2 \cdot F} \right] \ln \left[\frac{1 - \left(\frac{R \cdot T_{AN}}{2 \cdot F} \right) \left(\frac{t_{AN}}{D_{AN(eff)} \cdot y_{H_2}^0 \cdot P_{AN}} \right) j}{1 + \left(\frac{R \cdot T_{AN}}{2 \cdot F} \right) \left(\frac{t_{AN}}{D_{AN(eff)} \cdot y_{H_2O}^0 \cdot P_{AN}} \right) j} \right] \quad \text{Anode} \quad (7.15)$$

$$V_{Conc_CATH} \quad \text{Cathode} \quad (7.16)$$

$$= - \left[\frac{R \cdot T_{CATH}}{4 \cdot F} \right] \ln \left[\frac{\left(\frac{P_{CATH}}{\delta_{O_2}} \right) - \left\{ \left(\frac{P_{CATH}}{\delta_{O_2}} \right) - y_{O_2}^0 \cdot P_{CATH} \right\} \text{Exp} \left\{ \left(\frac{R \cdot T_{CATH}}{4 \cdot F} \right) \left(\frac{\delta_{O_2} \cdot t_{CATH}}{D_{CATH(eff)} \cdot P_{CATH}} \right) \right.}}{y_{O_2}^0 \cdot P_{CATH}}$$

where,

$$D_{AN(eff)} = y_{H_2O}^0 \cdot D_{H_2(eff)} + y_{H_2}^0 \cdot D_{H_2O(eff)} \quad (7.17)$$

$$D_{CATH(eff)} = D_{O_2(eff)} \quad (7.18)$$

$$\delta_{O_2} = \frac{D_{kd,O_2(eff)}}{D_{kd,O_2(eff)} + D_{O_2-N_2(eff)}} \quad (7.19)$$

where,

Ordinary diffusion coefficients of both binary reacting and product specie given by Fuller, Schettler, and Giddings (1966) having only about 5% mean error (304) is shown in Equation (7.20).

$$D_{ik} = \frac{10^{-7} \times (\sqrt[4]{T_{AN}})^7 \times \left(\sqrt{\frac{1}{M_i} + \frac{1}{M_k}} \right)}{P(\sqrt[3]{v_i} + \sqrt[3]{v_k})^2} \quad (7.20)$$

where i and k denotes gaseous specie that constitute the mixture of the binary gas i.e., anodic H₂-H₂O reaction and cathodic O₂-N₂ reaction, v denotes fuller diffusion volume i.e. H₂ (7.07), H₂O (12.7), O₂ (16.6) and N₂ (17.9). (303) and ' M_i and M_k ' denotes molecular mass of gaseous specie that constitute the mixture of the binary gas (kg/kmol).

And Equation (7.21) below determines the effective ordinary diffusion coefficient.

$$D_{ik(eff)} = \left(\frac{\varepsilon}{\xi} \right) D_{ik} \quad (7.21)$$

Where ε denotes electrodes porosity given as 0.5 (305), ξ denotes electrodes tortuosity given as 5.9 (305).

Likewise, Equation (7.22) calculate the Knudsen diffusion where ' r ' which denotes the pore radius of the electrode is given as $\left(\frac{1}{2000000} \right) m$ (298).

$$D_{kd,i} = \left(\sqrt{\frac{T_{AN}}{M_i}} \right) \cdot 97r \quad (7.22)$$

Moreover, the effective Knudsen diffusion is determined by using Equation (7.23) for both electrodes.

$$D_{kd,i(eff)} = \left(\frac{\varepsilon}{\xi} \right) D_{K,i} \quad (7.23)$$

Lastly, the Equation (7.24) was used for the determination of the overall effective diffusion coefficient of individual reacting and product specie.

$$\frac{1}{D_{i(eff)}} = \frac{1}{D_{ik(eff)}} + \frac{1}{D_{kd,i(eff)}} \quad (7.24)$$

- iii. Ohmic loss: This is the loss of voltage as a result of the resistance caused by flow of electrons in the electrodes (i.e. anode and cathode) and the interconnection and flow of ions in the electrolyte. The ohmic voltage loss is determined by employing the Equation (7.25) to (7.28) invented by (300).

$$V_{\Omega_{AN}} = [(\pi \cdot A \cdot D_m)^2 \rho_{AN} \cdot j] / [8 \cdot t_{AN}] \quad \text{Anode} \quad (7.25)$$

$$V_{\Omega_{CATH}} = [(\pi \cdot D_m)^2 \rho_{CATH} \cdot j] / [8 \cdot t_{CATH}] \cdot A[A + 2(1 - A - B)] \quad \text{Cathode} \quad (7.26)$$

$$V_{\Omega_{INTC}} = \rho_{INTC} \cdot j \cdot \pi \cdot D_m (t_{INTC} / w_{INTC}) \quad \text{Interconnection} \quad (7.27)$$

$$V_{\Omega_{ELECT}} = \rho_{ELECT} \cdot t_{ELECT} \cdot j \quad \text{Electrolyte} \quad (7.28)$$

Where πA denotes angular electrical contact given by the value $A = 0.804$ (300), πB denotes extent of angular contact associated to the interconnection, $B = 0.13$, D_m denotes the mean diameter of a cell given as 0.022m (306), ρ_i denotes the material (i) resistivity given by the following temperature dependent relation ($\Omega \text{ m}$), for anode: $2.98 \times 10^{-5} \exp(\frac{-1392}{T_{AN}})$, for cathode: $8.114 \times 10^{-5} \exp(\frac{600}{T_{CATH}})$, for electrolyte: $2.94 \times 10^{-5} \exp(\frac{10350}{T_{AN}})$, (307) for interconnection 0.025 (308), t_i denotes i thickness (m), i.e. For anode: 1×10^{-4} , for cathode: 2.2×10^{-3} , for electrolyte: 4×10^{-5} , for interconnection: 8.5×10^{-5} and w_{INTC} denotes width of the interconnection (m) given as 9×10^{-3} (309).

Therefore, the actual cell voltage was determined by subtracting the various losses discussed above from the Nernst reversible voltage as shown in Equation (7.29).

$$V = V_{NST} - [V_{ACTV} + V_{Conc} + V_{\Omega}] \quad (7.29)$$

Current (I) in Ampere (A) is given by:

$$I = 2FnH_{2,consumed} \quad (7.30)$$

AC power (P_{AC}) in watts (W) is equal to the DC power (P_{DC}) in watts (W) multiplied by the inverter efficiency. The equation for P_{DC} is given by:

$$P_{DC} = I \cdot V \quad (7.31)$$

Also, AC efficiency is given as:

$$AC \text{ efficiency} = \frac{P_{AC}}{nFuel_{in} \cdot LHV_{fuel}} \quad (7.32)$$

Where $nFuel_{in}$ denotes the molar flow rate (mols^{-1}) of the fuel, and the LHV_{fuel} denotes the lower heating value of the fuel (Jmol^{-1}).

7.4 Validation of the Model

The model was validated against three different studies (257,310,311), using similar input data as presented in **Table 7.2** and **Table 7.3** displays comparisons between the results obtained in this study and those from similar studies in the literature. As observed, the results in this study largely align with most of the reported data. The subtle discrepancy observed in the cell voltage V can be attributed to the fact that the author of study [12] employed a different approach for voltage computation.

Table 7.2: Input data for model validation

Parameter	Values
Fuel gas composition (%)	CH ₄ (81.3), C ₂ H ₆ (2.9), C ₃ H ₈ (0.4), C ₄ H ₁₀ (0.2), N ₂ (14.3) and CO ₂ (0.9)
Ejector operating pressure (atm)	3
SOFC anode pressure (atm)	1
Area of active site (m ²)	96.076
Number of cells (-)	1152
Input fuel temperature (°C)	200
Input air temperature (°C)	630
Operating temperature (°C)	910
Fuel utilisation factor (-)	0.85
Air utilisation factor (-)	0.19
Steam-to-carbon ratio (-)	2.5
DC power (kw)	120
Inverter efficiency (%)	92

They utilised a reference polarisation curve to semi-empirically develop a correlation for voltage calculation. Studies (312) have ascertain that the approach or the correlation may struggle with other available fuels.

Table 7.3: Model validation results

Parameter	Unit	(310)	(257)	(311)	This study
Cell Voltage	V	nr	0.70	0.68	0.69
Current density	Am ⁻²	1800	1780	1830	1750
Reformer temp.	°C	550	536	535	523
Reformer CH ₄ Conversion	%	15	25.9	25	25.7
Reformer heavy hydrocarbons conversion	%	100	100	100	100
Cathode inlet temperature	°C	nr	821	823	825
Combustion products temp.	°C	nr	1012	1012	1015
Stack exhaust temp	°C	847	834	834	835
Anode inlet gas composition	%	nr	H ₂ 27, CO 5.6, CH ₄ 10.1, H ₂ O 27.9, CO ₂ 23.1, N ₂ 6.2	H ₂ 26.9, CO 5.6, CH ₄ 10.4, H ₂ O 27.8, CO ₂ 23.1, N ₂ 6.2	H ₂ 22.9, CO 3.9, CH ₄ 5.9, H ₂ O 35.2, CO ₂ 26.4, N ₂ 5.7
Anode outlet gas composition	%	H ₂ 14, CO 5, H ₂ O 48, CO ₂ 28, N ₂ 5	H ₂ 11.6, CO 7.4, H ₂ O 50.9, CO ₂ 24.9, N ₂ 5.1	H ₂ 11.6, CO 7.4, H ₂ O 50.9, CO ₂ 24.9, N ₂ 5.1	H ₂ 6.88, CO 12.1, H ₂ O 55.6, CO ₂ 20.2, N ₂ 5.1
Cathode outlet gas composition	%	nr	O ₂ 17.7, N ₂ 82.3	O ₂ 17.7, N ₂ 82.3	O ₂ 17.7, N ₂ 82.3
Stack exhaust gas composition	%	O ₂ 16, N ₂ 77, H ₂ O 5, CO ₂ 2	O ₂ 15.9, N ₂ 77.3, H ₂ O 4.5, CO ₂ 2.3	O ₂ 15.9, N ₂ 77.3, H ₂ O 4.5, CO ₂ 2.3	O ₂ 15.9, N ₂ 77.3, H ₂ O 4.5, CO ₂ 2.3
Gross AC efficiency (LHV)	%	50	52	51	51

The approach used for the voltage computation herein is regarded more meticulous as the relations involve can tackle variations in operating pressure, operating temperature, gas compositions, property of materials and geometry of the cell, thus, can accommodate fuels with diverse properties. Other differences observed between the results of this study and those in [12] may arise from the differing methods employed to simulate the oxidant flow rate. In the present study, the flow rate is modelled based on a specified air utilisation factor, as outlined in Table 7.2. In contrast, the study referenced in [12] employs a heat balance approach, assuming a specific level of heat loss.

For further validation, the current study employs input parameters like fuel composition (H_2 : 0.34, N_2 : 0.01, H_2O : 0.257, CO : 0.16, CO_2 : 0.158, CH_4 : 0.074), air utilisation of 16.7%, fuel utilisation of 85%, and a steam-to-fuel ratio of 2.5, sourced from Doherty [35]. The comprehensive stream results of this model, displayed in Table 7.4, are in high agreement with those reported in (311) with highest standard deviation of 0.02.

Table 7.4: The streams properties for detailed flowsheet of **Figure 7.2** data captured by the developed SOFC model using the inputs from (311)

Stream Name	Temperature	Pressure	Mole Flows	Mole Fractions						
	°C	bar	kmolhr ⁻¹	H ₂	O ₂	CH ₄	CO ₂	H ₂ O	CO	N ₂
Fresh Fuel	200	1.01	4.99	0.34	0.00	0.07	0.16	0.26	0.16	0.01
Fresh Air	24.9	1.01	48.2	0.00	0.21	0.00	0.00	0.00	0.00	0.79
Fuel Heater Outlet	300	3.28	4.99	0.34	0.00	0.07	0.16	0.26	0.16	0.01
Ejector Outlet	586	1.09	8.73	0.21	0.00	0.04	0.21	0.41	0.12	0.01
Pre-reformer Inlet	586	1.09	8.73	0.21	0.00	0.04	0.21	0.41	0.12	0.01
Anode Inlet	576	1.09	8.93	0.30	0.00	0.03	0.26	0.33	0.07	0.01
Anode Outlet	910	1.09	9.47	0.03	0.00	0.00	0.27	0.62	0.07	0.01
Recycle	910	1.09	3.74	0.03	0.00	0.00	0.27	0.62	0.07	0.01
Post Combustion Inlet (PCI _{Spent_Fuel})	910	1.09	5.73	0.03	0.00	0.00	0.27	0.62	0.07	0.01
Post Combustion Outlet	910	1.09	51.9	0.00	0.16	0.00	0.04	0.07	0.00	0.73
HeatX Hot Inlet	997	1.09	51.9	0.00	0.16	0.00	0.04	0.07	0.00	0.73
HeatX Hot Outlet	832	1.09	51.9	0.00	0.16	0.00	0.04	0.07	0.00	0.73
HeatX Cold Inlet	630	1.09	48.2	0.00	0.21	0.00	0.00	0.00	0.00	0.79
Cathode Inlet	822	1.09	48.2	0.00	0.21	0.00	0.00	0.00	0.00	0.79
Electrochemically Transferred O ₂	822	1.09	1.69	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Preheated Cathode Outlet	822	1.09	46.5	0.00	0.18	0.00	0.00	0.00	0.00	0.82
Heated Cathode Outlet (PCI _{Spent_Air})	910	1.09	46.5	0.00	0.18	0.00	0.00	0.00	0.00	0.82

7.5 Results and discussions

7.5.1 Effect of fuel utilisation factor (U_f)

Figure 7.3 shows the effect of U_f on the AC efficiency, flow rate of the recirculated fuel, methane conversion, DC electricity output, and cell voltage of the SOFC at a constant fuel input flow rate of $4.99 \text{ kmol/hr}^{-1}$ and steam-to-carbon ratio of 2.5.

As observed, the cell voltage slightly decreases with U_f which can be attributed to the increase in voltage losses (such as activation, ohmic, and concentration) and a higher level of fuel depletion which also leads to increase the current density as observed in **Figure 7.4**.

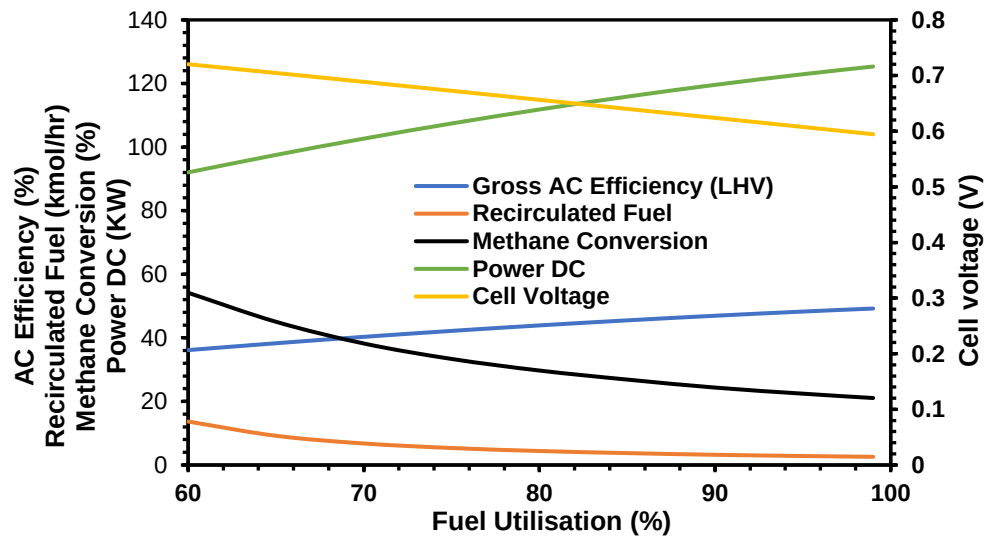


Figure 7.3: Effect of fuel utilisation factor on the AC efficiency, recirculated fuel, methane conversion, power (DC), and cell voltage

The AC Efficiency (LHV) increased by 10.9 percentage points over the U_f range investigated. This increase occurs because more energy from the fuel is converted into electricity due to higher hydrogen consumption in the electrochemical reaction.

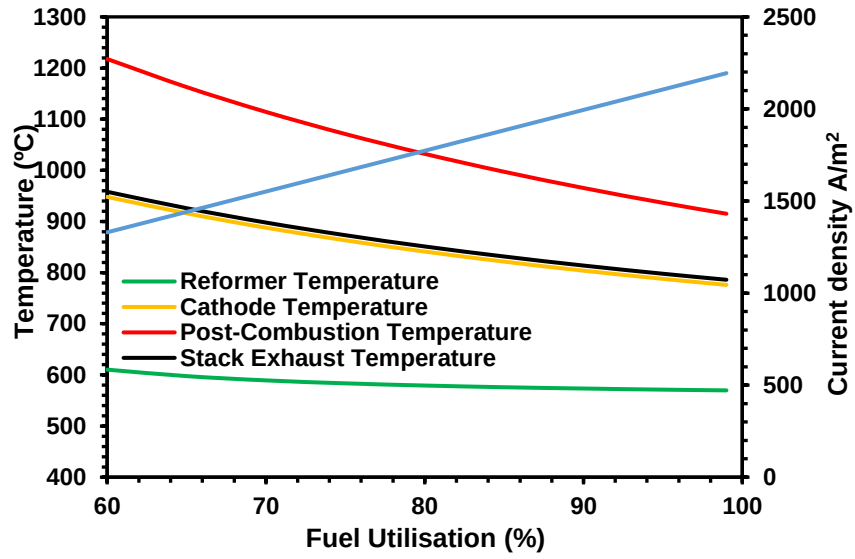


Figure 7.4: Effect of fuel utilisation factor on the reformer temperature, cathode temperature, post-combustion temperature, stack exhaust temperature and current density

The observed trend in cell voltage and AC efficiency aligns well with findings reported in several similar studies in literature (311,313). As observed in **Figure 7.3**, the mole flow of recirculated fuel decreases with U_f . This is attributed to a reduced need for fuel recirculation in order to maintain the specified steam-to-carbon ratio (S/C), owing to increased water content in the spent fuel, as depicted in **Figure 7.5**. Consequently, a reduction in the recirculation of high-temperature depleted fuel leads to a drop in the temperature at the pre-reformer, as evidenced by **Figure 7.4**.

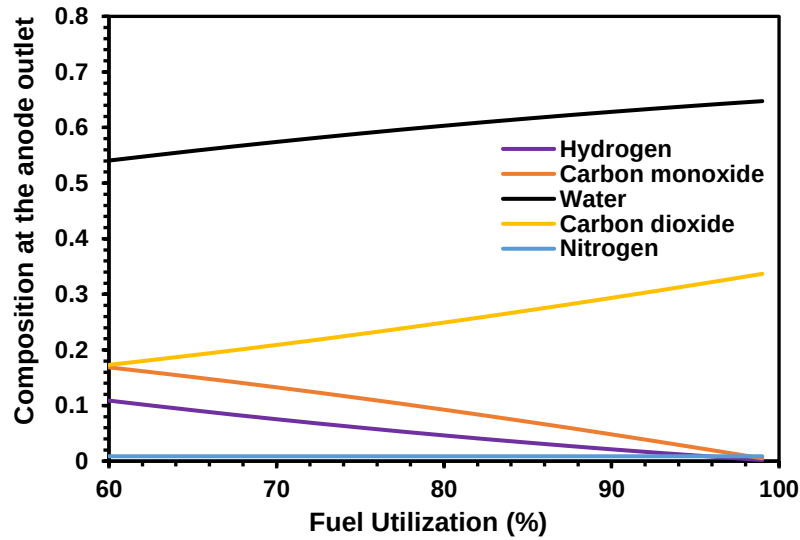


Figure 7.5: Effect of fuel utilisation factor on the gas composition at the anode outlet

Moreover, the methane conversion fraction decreases, as observed in **Figure 7.3**. The effect of lowered temperature (from 610.3°C to 569.7°C, see **Figure 7.4**) on methane conversion can be explained by the endothermic nature of methane steam reforming (via Equation (7.1)), meaning the forward reaction is less favoured as the temperature decreases. The temperatures of the cathode and stack exhaust are influenced by the post-combustion temperature, which in turn is governed by the quantity of fuel accessible for combustion. At lower U_f values, more fuel is available for combustion, resulting in higher temperatures. As U_f increases, indicating more fuel energy is converted to electricity, the temperatures decrease. Given these observations, it is advisable to run the SOFC stack at higher levels of fuel utilisation, yet not exceeding the threshold where concentration loss becomes unduly significant (a typical U_f value would be 0.85).

7.5.2 Effect of current density

Figure 7.3 depicts the effect of current density in the range of 440 to 4440 Am^{-2} on the cell voltage, AC efficiency, and AC power (@ inverter efficiency of 92%) of the SOFC at a constant fuel input flow rate of 4.99 kmolhr^{-1} , 85% fuel utilisation factor and steam-to-carbon ratio of

2.5. The cell voltage drops, that can be seen in **Figure 7.6**, are mainly due to increased voltage losses. Also, as shown in **Figure 7.6**, a parabolic relationship is observed between the current density and the AC efficiency as the current density is being varied from 440 to 4440 Am^{-2} , with the peak AC efficiency of 65% occurring at a current density of 3190 Am^{-2} . This, however, contrasts with the trends observed in the study reported by Doherty et al. (311). The discrepancy arises due to the uneven increase in parasitic power and energy input.

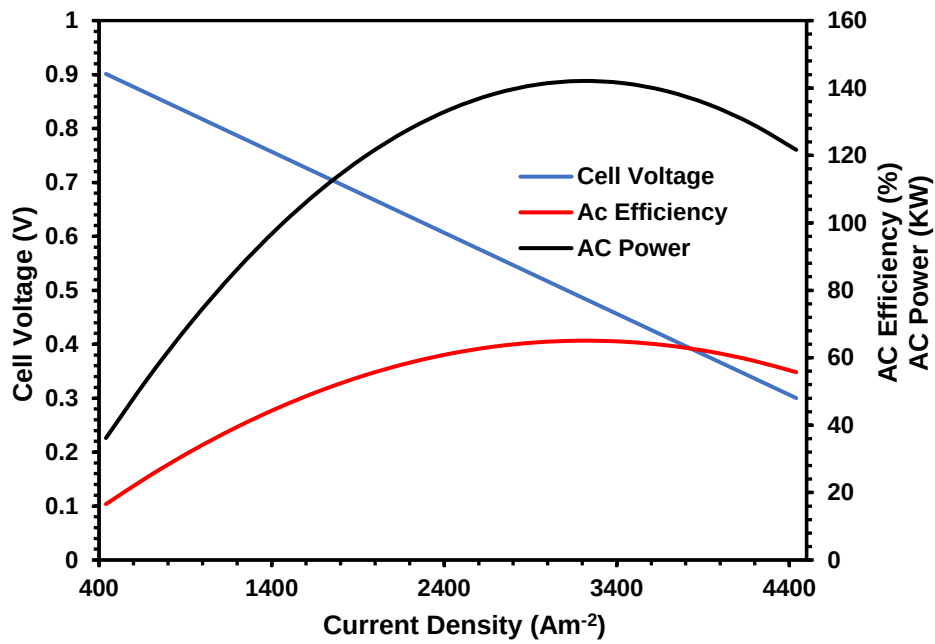


Figure 7.6: Effect of fuel utilisation factor on the cell voltage, AC efficiency and AC power

In the present study, the SOFC is modelled to utilise a constant fuel flow rate, whereas the study (311) models the SOFC in a manner that varies the fuel flow rate until a desired DC power output is achieved. The AC power, as depicted in **Figure 7.6**, is also observed to exhibit a parabolic relationship with the current density. The peak AC power of 142 kW occurs at a current density of 3190 Am^{-2} .

However, it is common practice to operate fuel cells to the left of the peak AC power. While high voltage and AC efficiency are desirable for operational costs, high AC power is also

beneficial in terms of the capital costs of the SOFCs. A trade-off must exist among AC efficiency, AC power, and cell voltage. Based on **Figure 7.6**, it is advisable to operate the fuel cell at current densities ranging from 1690 to 1940 Am^{-2} . This corresponds to a cell voltage of 0.68 - 0.71 V, an AC efficiency of 50.3 – 54.8%, and an AC power output of 110.0 – 119.7 kW.

7.5.3 Effect of steam-to-carbon (S/C) ratio

The effects of varying the steam-to-carbon (S/C) ratio at the reformer inlet on AC efficiency, current density, cell voltage, recirculated fuel, anode inlet gas temperature and composition, and AC power in the SOFC model are investigated at 85% fuel utilisation. Maintaining an optimal S/C ratio at the reformer inlet of a high-temperature fuel cell like SOFC is essential for preventing carbon formation on its electrodes.

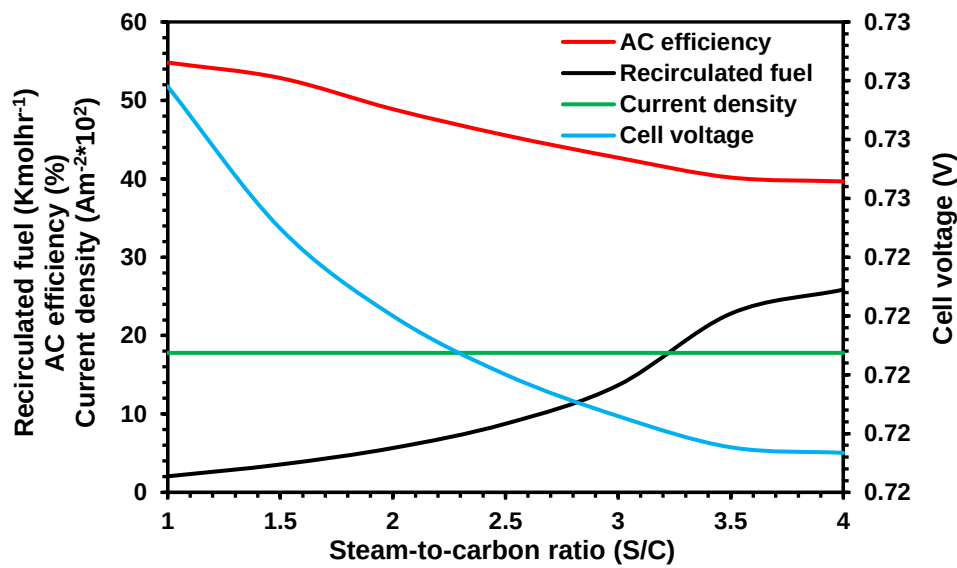


Figure 7.7: Effect of steam-to-carbon ratio on the AC efficiency, recirculated fuel, current density, and cell voltage

As the S/C ratio increases, both the cell voltage and AC efficiency, as shown in **Figure 7.7**, are negatively affected as observed. This is attributed to changes in the anode temperature (see **Figure 7.8**) and gaseous component partial pressures (see **Figure 7.9**), which result in a decreased Nernst voltage and increased voltage losses. Therefore, it is advisable to operate the

SOFC at low S/C ratio. This observation is consistent with findings from similar studies in the literature (311,313–315). The S/C ratio was observed to impact on the reformer inlet temperature, as shown in **Figure 7.8**. The increased flow rate of recirculated fuel, depicted in **Figure 7.7**, enhances heat transfer, causing the reformer inlet temperature to rise from 568 to 578 °C across the range of the S/C ratio investigated. This observation aligns with findings from Mahisanana et al. (316), who suggested that an S/C ratio of 2.5 yields better SOFC performance outcomes.

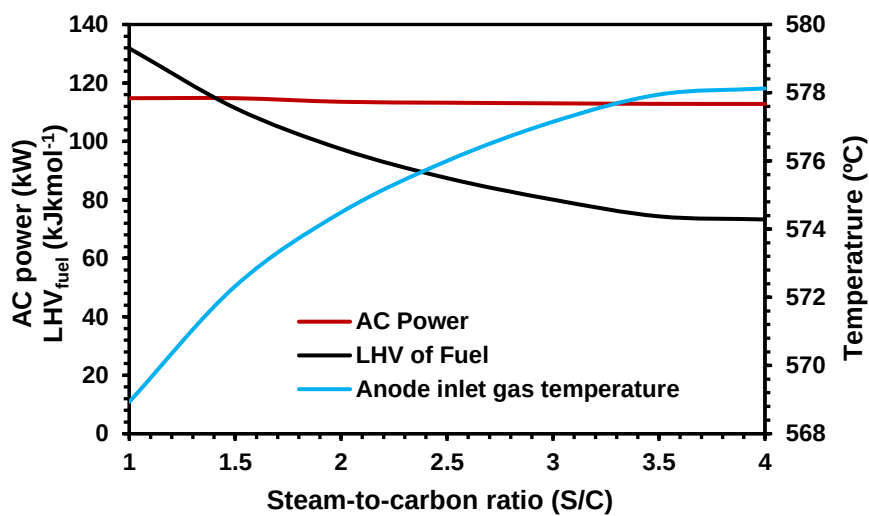


Figure 7.8: Effect of steam-to-carbon ratio on the AC power, LHV of gas composition at the reformer inlet, and anode inlet gas temperature

Figure 7.9 shows the impact of S/C ratio on the anode inlet gas composition. As observed, an increase in the S/C ratio leads to a higher percentage of steam and carbon dioxide, which in turn reduces the percentage of hydrogen and carbon monoxide, adversely affecting SOFC performance. This can be explained by the fact that excess steam and carbon dioxide dilute the reactants and negatively affect the LHV of the anode inlet gas composition (see **Figure 7.8**). This dilution causes electrode flooding, leading to issues in reactant transport and a decrease in overall reaction rates. Consequently, results in a decline in AC power, as observed in **Figure 7.8**. Based on the findings of the current study, it is recommended to operate the SOFC stack

at a relatively low S/C ratio, while ensuring that the level is adequate to prevent issues related to carbon formation.

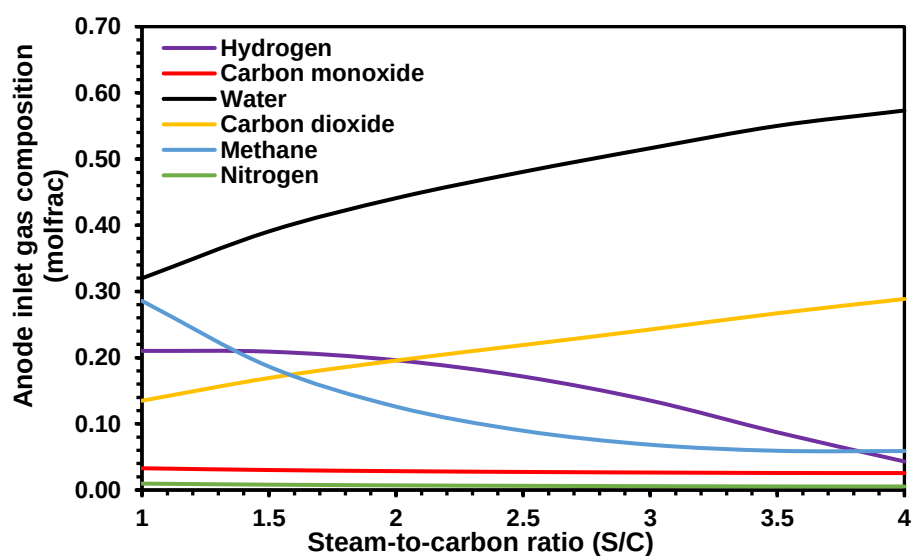


Figure 7.9: Effect of steam-to-carbon ratio on the anode inlet gas composition

CHAPTER 8: MODELLING AND SIMULATION OF A SOLID OXIDE ELECTROLYSER FOR CO-ELECTROLYSIS OF STEAM AND CO₂ FOR PRODUCTION OF SYNGAS

8.1 Introduction

Building upon the content in Chapter 7, which addressed the simulation and modelling of solid oxide fuel cells (SOFCs), operating the SOFC in reverse mode as solid oxide electrolyzers (SOEs) essentially involves the co-electrolysis of steam and CO₂ to produce syngas. However, owing to the promising capacity of SOEs for large-scale syngas or hydrogen production, there has been significant interest, leading to the launch of multiple initiatives by the United States Department of Energy (DOE) (317). The integration of SOEs with diverse energy sources, both renewable and non-renewable powered energy plants, is also attracting increased attention as a strategy to enhance the production efficiency of syngas (318,319).

A range of mathematical models have emerged, focusing on simulating the various physical and chemical behaviours within SOEs (214,219,320–322). Research indicates notable differences in the transport phenomena of SOEs as compared to SOFCs, suggesting that findings specific to SOFCs might not translate seamlessly to SOEs (323). Beyond the scope of steam electrolysis for hydrogen generation outlined in Chapter 4, the current chapter extends into the realm of combined steam and CO₂ co-electrolysis modelling and simulation. Additionally, there has been a confirmation through practical experiments by multiple research teams on the viable co-electrolysis of H₂O and CO₂, which paves the way for the syngas generation (324–326).

The co-electrolysis of steam and carbon dioxide in SOEs is more complex compared to the individual electrolysis of the feedstocks. This complexity is due to the potential reactions outlined in Equations (8.1) - (8.4) that could occur at the cathode (58).





As mentioned earlier, and in line with the decarbonisation and power-to-gas technology plant proposed in Chapter 1, this chapter introduces model development aimed at examining the intertwined heat and mass transfer processes together with the chemical and electrochemical reactions occurring within an SOE during the co-electrolysis of H₂O and CO₂. The model is based on, and an extension of, the previous models for H₂O electrolysis [Chapter 4].

Modelling outcomes indicate that in the co-electrolysis process, the generation of CH₄ through reversed steam reforming, as described in Equation (8.2) and (8.4), tends not to be advantageous. On the other hand, depending on the specific operating conditions, the reversible water gas shift reaction (WGSR) may play a key role in enhancing CO production.

8.2 System Process

The operational principle of a SOE for steam and carbon dioxide co-electrolysis starts when an electric current is applied across the electrodes, which are separated by a ceramic matrix saturated with yttria-stabilised zirconia (YSZ) electrolyte as shown in **Figure 8.1**. A Mixture of carbon dioxide, steam, hydrogen and or carbon monoxide, is supplied to the cathode channel, while air is introduced at the anode channel. Generally, the possible reactions expected at the porous cathode electrode, which depend on the operating conditions (i.e. based on kinetic values that could be obtained at elevated temperatures in the presence of Ni catalyst (327)) include both the reversible methanation reactions (RMR) as shown in Equations (8.2) - (8.4) and the reversible water gas shift reaction (WGSR) shown in Equation (1.7). The carbon dioxide and steam molecules migrate to the triple phase boundary (TPB) at the interface between the cathode and the electrolyte where both carbon dioxide and water splitting reaction

occurs to form CO, H₂, and O²⁻ ions as detailed in Equations (1.4) and (1.5). The O²⁻ ions are conducted through the ceramic matrix electrolyte to reach the TPB at the anode-electrolyte interface where they release the electrons to form oxygen molecules, as outlined in Equation (8.7).

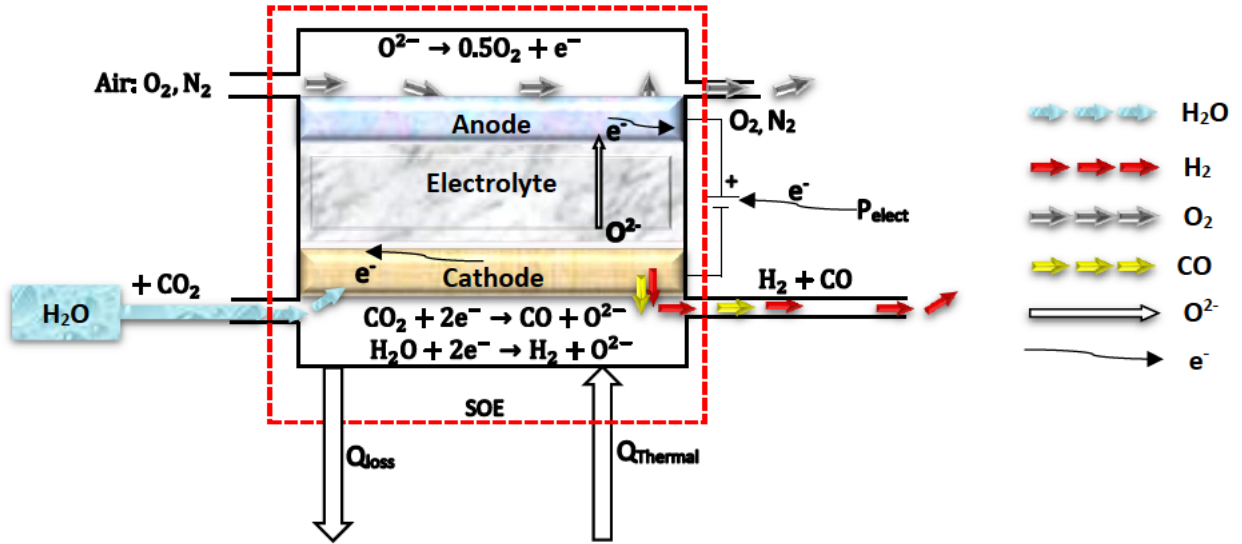
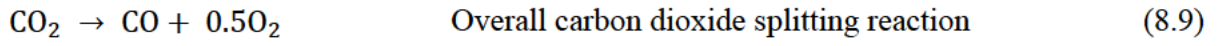
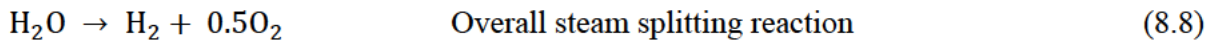
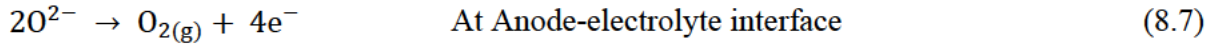
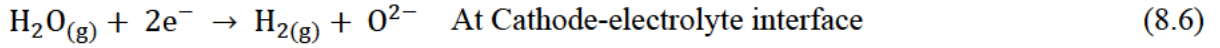
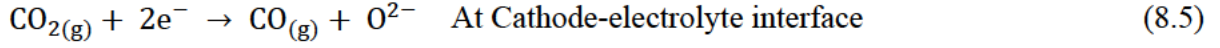


Figure 8.1: Solid oxide electrolyser for co-electrolysis of H₂O/CO₂

8.3 Simulation method

In the model, contrary to the established practice for the SOE model for steam electrolysis presented in Chapter 4 of this thesis, the boiler and the electric heater are not included in the Balance of Plant (BoP). This is because the hot exit streams from the SOFC anode will add to a mixture that is directed to the SOE cathode discussed in this chapter. Similarly, the exit

streams from the SOFC cathode will be fed to the SOE anode (see **Figure 1.2**). Pressure drops in the connecting piping are ignored at this stage.

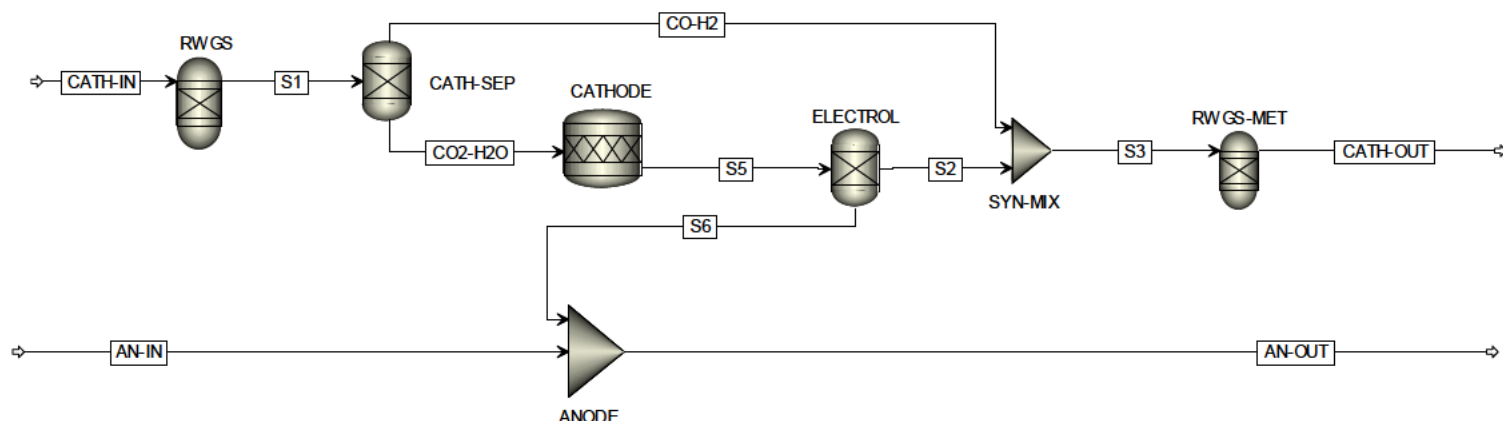


Figure 8.2: SOE subsystem flowsheet.

The stream (CATH-IN in **Figure 8.2**), containing the feed, is first directed to a RGibbs reactor, namely: 'RWGS' block, to simulate the equilibrium-based reverse water gas shift reaction as shown in Equation (1.7). Hydrogen gas is added to the feed to prevent oxidation of the nickel on the cathode (224). The exit stream 'S1,' primarily consisting of $\text{CO}_2/\text{H}_2\text{O}$, is then fed into a separator 'CATH-SEP' which routes $\text{CO}_2/\text{H}_2\text{O}$ to the 'CATHODE' block. The ASPEN RSTOIC reactor model is employed to simulate the cathodic electrochemical reaction of steam and carbon dioxide at the specified temperature. The overall cell reactions, as outlined in Equations (8.8) and (8.9), are considered in the 'CATHODE' block. For simulation purposes, the cathode (fuel electrode) discharge stream 'S5' is processed through a separator 'ELECTROL' block to separate the syngas and oxygen. The oxygen is subsequently channelled to the anode, simulating the migration of O^{2-} ions through the electrolyte.

The other stream 'S2', which carries syngas, is combined with additional syngas in the 'SYN-MIX' block, which also receives syngas from 'CATH-SEP'. The 'SYN-MIX' block's exit stream is then introduced to another RGibbs reactor, 'RWGS-MET,' for further equilibrium-based reverse water gas shift and methanation or steam reforming reactions as described by Equations (1.7) - (8.4). The sweep gas, labelled as "AN-IN," facilitates the transfer of oxygen produced

at the anode (oxygen electrode) surface, as shown in Equation (8.7). the sweep gas can be either oxygen, steam, or air, in this case, oxygen is utilised.

8.4 Computation of electrical and thermal energy requirements

8.4.1 Electrochemical model

As previously discussed, the electrochemical model for the co-electrolysis of CO₂/H₂O in an SOE builds upon and extends the models previously developed for H₂O electrolysis (**refer to chapter 4**).

During operation, the voltage demand of the SOE can be estimated using the Equation (8.10):

$$V = E_{eq} + E_{Tloss} \quad (8.10)$$

$$E_{TLoss} = E_{act} + E_{conc} + E_{ohmic} \quad (8.11)$$

$$E_{eq} = \sum E_i \quad (8.12)$$

Where E_{eq} is the equilibrium potential, E_{Tloss} is the total overpotential, E_{act} is activation overpotential, E_{conc} is concentration overpotential, E_{ohmic} is ohmic overpotential and i denotes CO or H₂. For detailed explanations of activation overpotential, concentration overpotential, and ohmic overpotential, please refer to Chapter 4.

The equilibrium potential is the requisite minimum voltage for initiating the electrolysis process (328). Given that, multiple electrochemical reactions take place at the TPB, the mixed potential theory is employed to determine the equilibrium voltage. This accounts for the combined effects of the potentials arising from co-electrolysis of both H₂O and CO₂ as described in Equation (8.13). It is postulated that gas molecule adsorption on the electrode surface is consistent with the Langmuir isotherm model, which suggests that the presence of unoccupied sites has no impact on the equilibrium voltage. The surface coverage of specie j ,

denoted as θ_j , is determined using a variant of the Langmuir adsorption isotherm, as outlined in Equations (8.14) and (8.15) (328,329).

$$E_i = \theta_j \left[\frac{-\Delta G_{f,j}}{2F} + \frac{RT}{2F} \ln \left(\frac{p_i (p_{O_2})^{\frac{1}{2}}}{p_j} \right) \right] + \theta_{O_2} \left[\frac{RT}{4F} \ln \left(\frac{p_{O_2}^{Cathode}}{p_{O_2}^{Anode}} \right) \right] \quad (8.13)$$

$$\theta_j = \frac{K_j \cdot p_j}{\sum_l K_l p_l}, \quad j \neq l \quad (8.14)$$

$$K_j = K_j^0 \exp \left(\frac{Q_j}{RT} \right) \quad (8.15)$$

Where K_j denotes the adsorption constant of species j , p_j denotes the partial pressure of species j , K_j^0 is the standard adsorption constant of species j , Q_j denotes the enthalpy of adsorption, j denotes CO₂ and H₂O, and R and T are the gas constant and temperature, respectively, as previously defined. Since the partial pressures of all reacting and product species are included in Equation (8.13), E_{conc} are implicitly accounted for in the equilibrium voltage (320). The ohmic overpotential is estimated using the relation employed in chapter 4. For E_{act} , Equation (8.16) and (8.17) was employed.

$$E_{act} = \sum E_{act,i,x} \quad (8.16)$$

$$E_{act,i,x} = \frac{RTJ_i}{n_i F J_{i,x}^0} \quad (8.17)$$

Where x denotes cathode and anode.

The net thermal energy demand can be estimated using Equation (8.18):

$$Q_{Thermal} = Q_{T\Delta S} - Q_{Gen} \quad (8.18)$$

8.4.2 Validation of the model

The SOE model for Co-electrolysis was validated using experimental data from Torrell et al ., (330), who experimentally explored the Co-electrolysis of steam and CO₂ in full-ceramic

symmetrical SOEs. The cell used in the study consisted of a thin layer of $\text{Yb}_{0.6}\text{Sc}_{0.4}\text{SZ}$ with diameter of 19.7 mm and thickness of 100 μm as electrolyte, and $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ as fuel and air electrode.

Table 8.1: Model input parameters for validation

Model input parameters	Value	Unit	Ref
Operating temperature, T	850	$^{\circ}\text{C}$	(330)
Operating pressure, P	1	bar	(330)
Exchange current density for H_2 of the anode ($j_{0,an-H_2}$)	2.08×10^4	Am^{-2}	(224)
Exchange current density for H_2 of the cathode ($j_{0,cat-H_2}$)	2.24×10^4	Am^{-2}	(224)
Exchange current density for CO of the anode ($j_{0,an-CO}$)	8.32×10^3	Am^{-2}	
Exchange current density for CO of the cathode ($j_{0,cat-CO}$)	8.96×10^3	Am^{-2}	
Activation Energy of the cathode ($E_{a,cat}$)	100	kJmol^{-1}	(218)
Activation Energy of the anode ($E_{a,an}$)	120	kJmol^{-1}	(218)
Standard adsorption constant of H_2O	9.25		(329)
Standard adsorption constant of CO_2	2.27		
Enthalpy of adsorption of H_2O	13.2	kJmol^{-1}	
Enthalpy of adsorption of CO_2	18.8	kJmol^{-1}	

The cell was maintained at a constant temperature of 850 $^{\circ}\text{C}$ and pressure of 1 bar, with 50% argon as the sweep gas at the air electrode at a flow rate of 140 mL min^{-1} , and a mixture of carbon dioxide, steam, and hydrogen (mole fractions 0.47, 0.47, 0.06 respectively) at the fuel electrode with a flow rate of 140 mL min^{-1} . Table 8.1 list the input parameters for the model, while **Figure 8.3** shows comparison of the model predictions and experimental polarisation curves.

The relative errors ranged from 0.01% to 13.17%. It can be observed that the model overestimated the open-circuit voltage (OCV) in regions where the activation overpotential at the cathode is dominant, primarily at lower current densities, as shown in **Figure 8.3**.

Furthermore, overall, a correlation coefficient of 0.996 was estimated, indicating a reasonable agreement between the model's predictions and the experimental data. Consequently, the model demonstrates good performance when compared to experimental data, providing confidence in its predictive capabilities and its use in the overall power to gas plant proposed in Chapter 1.

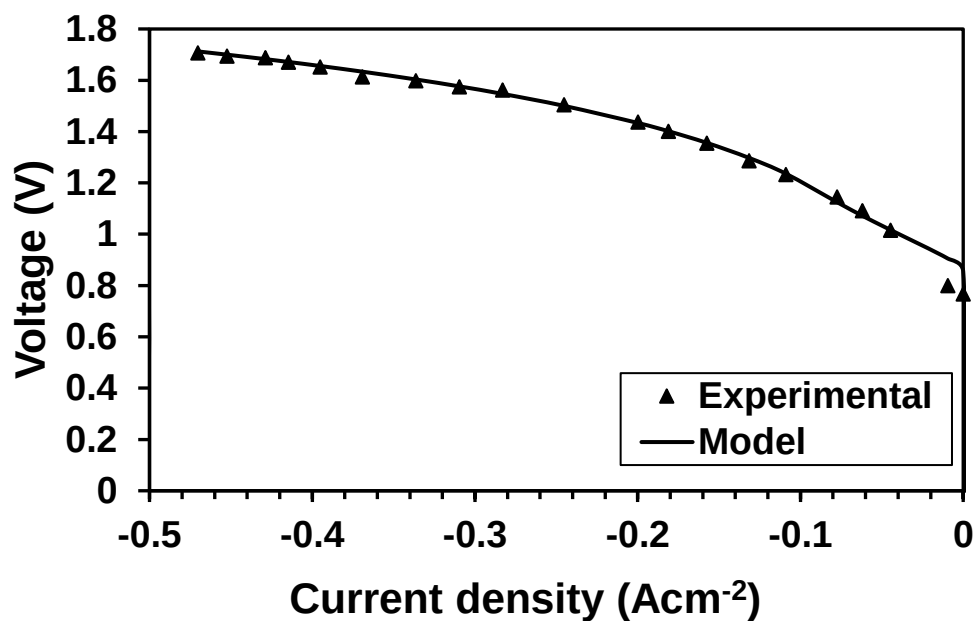


Figure 8.3: Model predictions and experimental polarisation curves (experimental data from (330)) The correlation coefficient of model and experimental data was 0.996

8.5 Results and discussion

8.5.1 Effect of Operating Pressure

Figure 8.4 and **Figure 8.5** displays the effect of operating pressure on the cell voltage and cathode outlet composition of an SOE respectively, at 850°C, inlet feed gas composition (mol fraction): H₂ 0.1, CO₂ 0.3, H₂O 0.6 and current density of -4675.7 Am^{-2} . The cell voltage showed an increase of up to 4.6 % when the operating pressure was increased from 1 to 10 bar. This increase can be attributed to enhanced gas-phase diffusion within the porous electrode,

caused by increased pressure. This enhancement boosts the availability of steam and CO₂ at the active reaction sites, thereby increasing the cell voltage. This finding aligns with the observations reported by other research teams (331). As evident from **Figure 8.5**, the mole fraction of H₂ in the cathode outlet stream is markedly greater than that of CO.

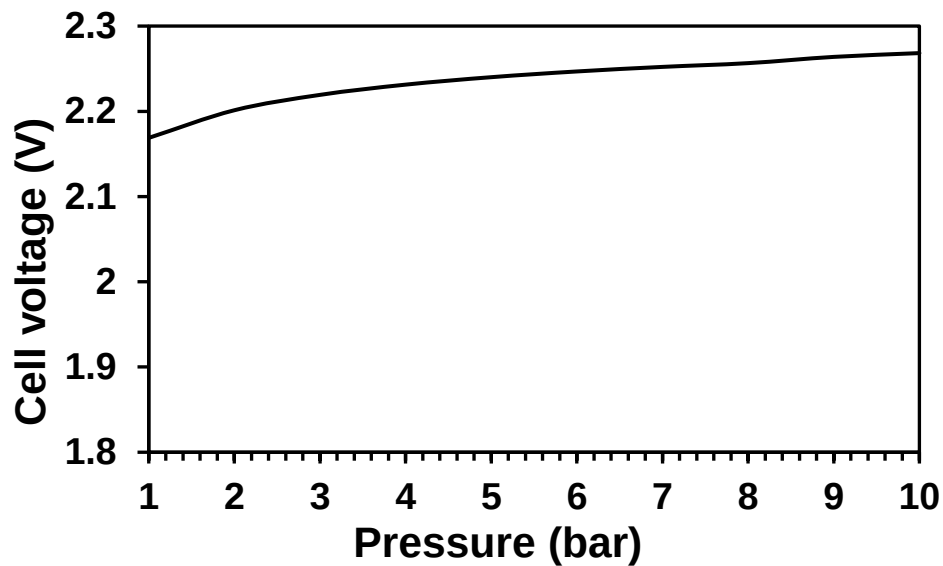


Figure 8.4: Effect of operating pressure on the cell voltage

This disparity can be attributed to the faster kinetics of steam electrolysis, in contrast to the slower electrochemical reaction of CO₂ (332,333). At elevated pressures, an increase in methane formation is observed, which can be traced back to Equations (8.2) - (8.4). This higher occurrence of CH₄ production at high pressures is due to the fact that the Sabatier reaction works better at higher pressures, a finding that has also been experimentally validated by numerous studies in the literature (334–336).

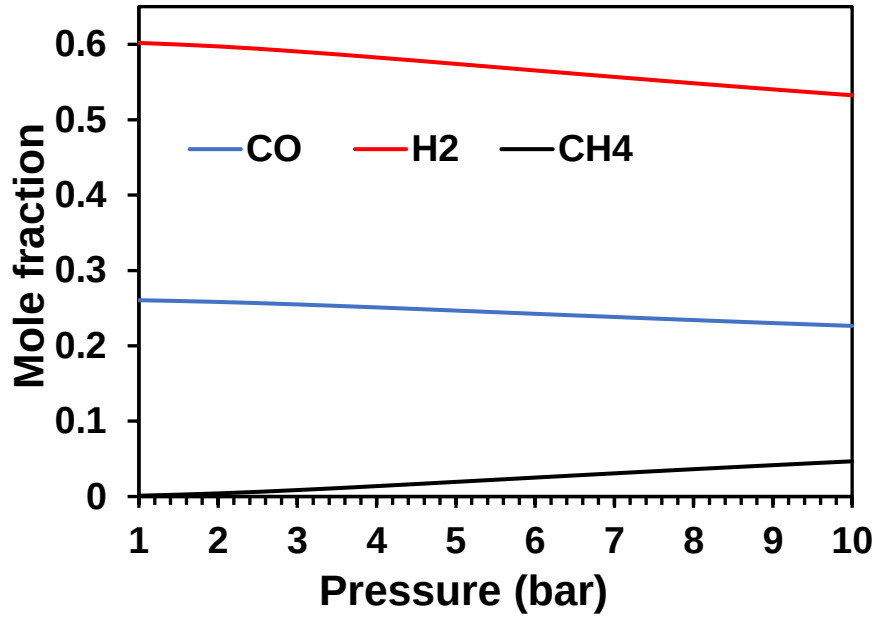


Figure 8.5: Effect of operating pressure on the cathode outlet composition

8.5.2 Effect of Cell Temperature

Figure 8.6 illustrates the impact of increasing cell temperature on the equilibrium mole fraction composition of the cathode outlet stream within the temperature range of 650 – 1050 °C and an inlet feed gas composition of (mole fraction): H₂ 0.1, CO₂ 0.3, H₂O 0.6. It is observed that, as shown in **Figure 8.6**, while the mole fractions of CO and H₂O exhibit an increase, the mole fractions of CO₂ and H₂ show a corresponding decrease. This trend is attributed to the increasing equilibrium constant, K_{eq} , (Equation (8.19)) as evident from **Figure 8.7**. Additionally, the total mole flow (kmol/hr) of CO + H₂ increases by 4.1% across the examined cell temperature range, as depicted in **Figure 8.7**. Hence, a higher operating cell temperature positively impacts the H₂O/CO₂ co-electrolysis process, both by increasing the electrochemical efficiency and lowered the energy demand.

$$K_{eq}(T) = \frac{y_{CO} \cdot y_{H_2O}}{y_{CO_2} \cdot y_{H_2}} \quad (8.19)$$

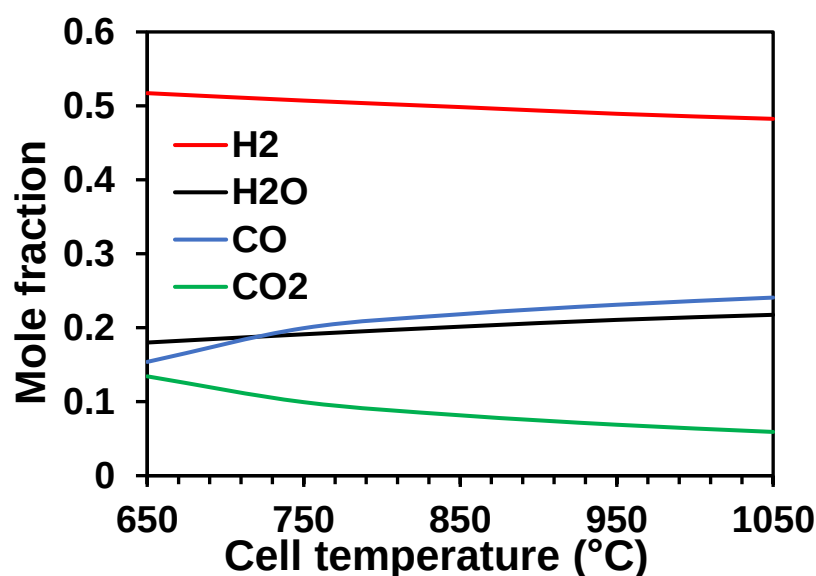


Figure 8.6: Effect of cell temperature on the equilibrium mole fraction of cathode outlet stream composition

As mentioned above, the observed trend of an increase in the mole fraction of CO produced, coupled with a decrease in that of H₂ as the operating temperature is increased, is likely due to the distinct production mechanisms for each gas. H₂ is primarily generated via the steam splitting reaction, as shown in Equation (8.8), while CO is predominantly produced through the RWGS reaction, as indicated in Equation (1.7), since it's a temperature-dependent process, thus creating a competition between H₂ and CO production. Optimal condition for co-electrolysis feeding a methanation reactor.

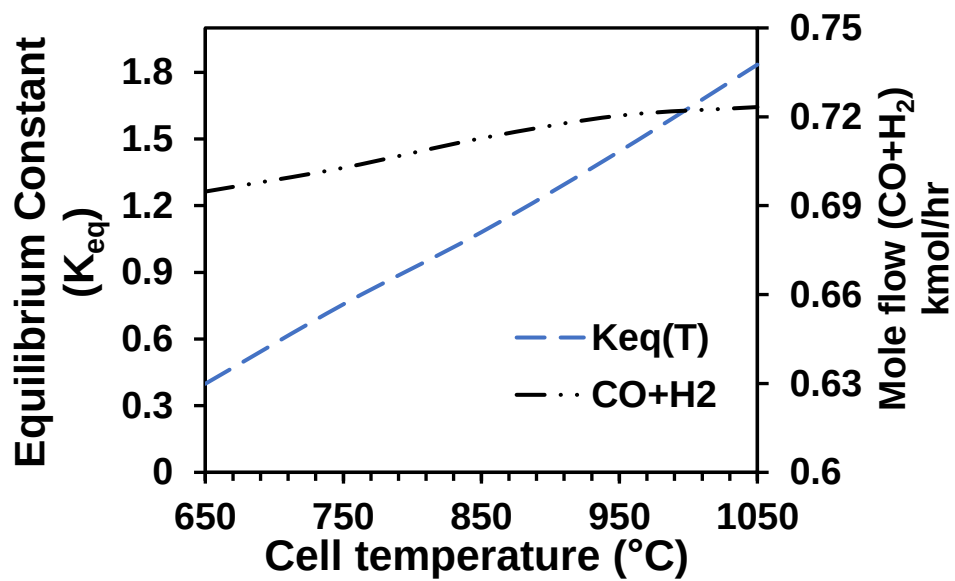


Figure 8.7: Effect of cell temperature on the equilibrium constant (K_{eq}) and the total mole flow (kmol/hr) of CO+H₂ in the cathode outlet

CHAPTER 9: THERMODYNAMIC AND ECONOMIC ASSESMENT OF A FUEL-CELL-BASED INTEGRATED POWER-TO-GAS ENERGY SYSTEM

9.1 Introduction

The UK and the EU have set ambitious goals to lower carbon dioxide emissions across various sectors by 2050 (337). Key areas of focus include energy generation, transportation, and home heating towards more sustainable practices. While there are numerous technological solutions available for carbon capture, transportation, and storage (CCS), these initiatives often face public resistance, especially regarding the transport and storage aspects of the CCS process. In line with these objectives, the UK's Net Zero Strategy includes plans to discontinue the sale of new petrol and diesel vehicles by 2030. Furthermore, by 2035, it is expected that all new vehicles will produce zero emissions of carbon dioxide from their exhausts (338).

The EU has increased its renewable energy target to 30% by 2023, an increase from the 20% goal set for the year 2020. Their renewable energy sector primarily relies on wind and solar power, which are inherently variable and experience fluctuations in production both daily and seasonally. To address the challenges of both carbon dioxide utilisation and the storage of energy derived from renewable sources, the implementation of PTG technology is being suggested. As the concept exploration of hydrogenation of carbon dioxide can be dated back to the year 1902 (339), the economic viability for mass-producing synthetic natural gas (SNG) only became a consideration more when the perception of dwindling availability and increasing cost of natural gas, coupled with a growing need to effectively utilise carbon dioxide and store excess energy generated from renewable sources emerged (339). In response to these needs, some EU countries have seen the development and initiation of several PTG projects. These systems, which are powered by renewable energy, are capable of producing gases such as CH_4 and H_2 . A notable example is the 6 MWel of electricity pilot plant developed in Germany by Audi at Werlte (340). An advanced, comprehensively integrated energy system capable of

supplying electricity, producing methane gas, and generating useful heat for local heating networks, among other utilities, could play a crucial role in the decarbonisation of the energy system. This would contribute significantly to helping the UK and EU to meet their ambitious targets of reaching net zero CO₂ emissions by 2050.

Praseeth et al. (341) investigated the HELMETH project, a SOE-based PTG system, observing an 85% overall process efficiency. Paolo et al. (342) focused on the University of California, Irvine's microgrid system, exploring the integration of a modular PTG system with SOE, highlighting its potential in absorbing almost 80% excess electricity from renewable sources and estimating its hydrogen production capability. Jakub et al. (343) studied PTG integration with SOE, and reported the system was capable of achieving an electrical efficiency of up to 74%. Easa et al. (344) analysed a PTG system incorporating a SOFC, SOE and a methanation unit, achieving a 58% energy storage efficiency. Zihang et al. (345) explored an electricity-H₂ energy system using a reversible solid oxide fuel cell, examining the impact of hydrogen injection into natural gas pipelines and the benefits of PTG with pipeline storage for renewable integration. Fabio et al. (346) assessed the coupling of a PTG plant of 30% utilisation factor with the electric residual profile, noting the feasibility of separating the electrolyser and methanation unit using a hydrogen storage tank and achieving overall energy efficiency of 77%. Xiaoyi et al. (347) explored a PTG and SOFC/gas turbine system, achieving 67% efficiency. Their multi-energy system model, optimised for low wind curtailment (0.63%) and high renewable penetration (90.1%), had a life cycle cost of £2,468,093.

Milewski et al. (348) proposed enhancing PTG systems using high-temperature electrolysis and a MCFC for carbon dioxide capture, achieving over 90% carbon dioxide separation and 35% electric efficiency, reducing hydrogen production energy by 25%. And lastly, Samiran et al. (349) developed an integrated energy hub combining SOFC, MCFC, PEM electrolyser, and

methanol production, achieving 322 kW power, 766.4 kW heat, 0.024 kg/s methanol, and 0.0362 kg/s oxygen with 86 % energy and 59 % exergy efficiency.

Drawing conclusions from the preceding discussions, it is evident that research on integrating SOEs for both steam and co-electrolysis, MCFC (for separation of CO₂), SOFC, and a methane production plant into a cohesive PTG system which is proposed in this thesis is limited. The system is capable of producing not only electrical energy and CH₄ but also O₂, CO₂, biomethane, and thermal energy for district heating networks. The purpose of this thesis corresponds with the seventh UN Sustainable Development Goal, (SuSDG) emphasising 'Clean Energy' (350). To aid in achieving the SuSDGs, herein, we explore a comprehensive analysis of a high temperature fuel cells-based integrated power system that not only generates various energy vectors but also produces economically and industrially valuable by-products. In pursuit of the SuSDGs, this research opens new avenues for various engineering fields by integrating a sustainable practice into the project designs. Furthermore, the role of carbon Capture, Utilisation, and Storage (CCUS) within the circular economy, in relation to meeting the SuSDGs, is associated with both energy and environmental concerns.

This part of the study presents an in-depth analysis of the system's thermodynamics, including the energy, exergy, and economic assessments of an innovative power-to-gas-based energy system aimed at the decarbonisation of power generation sector and heating networks. **Figure 1.2** in Chapter 1 of this thesis illustrates the concept of the fuel-cell-based power-to-gas integrated energy system for the decarbonisation of the energy generation sector.

The system produces electrical energy and methane gas, which not only aids in making the energy sector more eco-friendly but also fulfils regular home energy demands. Additionally, the thermal energy generated can contribute to the decarbonisation of the heating network.

The present study offers key advancements which include:

- Development of an innovative power-to-gas integrated energy system combining SOEs, MCFC, SOFC, and a methanation unit.
- Achieving over 85% CO₂ separation using an MCFC for upgradation of raw biogas and methane production.
- Conducting a comprehensive techno-economic analysis on the developed fuel-cell-based Power-to-Gas integrated energy system, focusing on both its thermodynamic efficiency and economic viability for decarbonising energy generation and district heating networks.
- Leveraging in-situ CO₂ for Power-to-Gas technology through the upgradation of raw biogas.

9.2 Methodology

9.2.1 The proposed process

As initially proposed in Chapter 1 of this thesis, water and treated raw biogas—specifically, biogas devoid of impurities such as H₂S, halogenated compounds, and H₂O—are supplied to the cathodes of SOE₁ and MCFC, respectively, as depicted in **Figure 9.1**. Recall from Chapter 6 that this thesis presented the integration of an SOE₁ with the MCFC for biogas upgrading. In this context, biogas upgrading serves as the unit supplying CO₂ to the power-to-gas system. Expanding on what was presented in Chapter 6, the MCFC anode outlet undergoes complete combustion in a post-combustion chamber, converting any unreacted H₂ and CO into H₂O and CO₂.

Methane gas from the storage is supplied to the anode of the SOFC, while the effluent from the SOFC anode, mainly consisting of CO₂ and H₂O, is directed to the SOE₂. Consequently, this sequence of operations produces syngas (comprising CO and H₂), which is then channelled into the methanation reactor. The integration of the units and their interconnections,

particularly through the use of heat exchangers, allows for the extraction of heat from stream outlets. This heat is utilised for the production of hot water at 80°C, which is then supplied to the district heating network. Further details on this process will be elaborated upon in the subsequent sections.

9.2.2 Simulation

The detailed model development of the SOE1, MCFC, SOFC, and SOE2 subsystems has already been presented in Chapters 4, 5, 7, and 8 of this thesis, respectively. Each model was individually validated using corresponding data from the literature. Every subsystem has its own flowsheet and auxiliary units. In this chapter, we integrate all these subsystems along with the methanation reactor to propose a novel power-to-gas energy system. The basic assumptions used in the modelling and simulation of the methanation reactor will be discussed in this subsection. The coupled model enables the simulation of the Balance of Plant (BoP), as depicted in **Figure 9.1**.

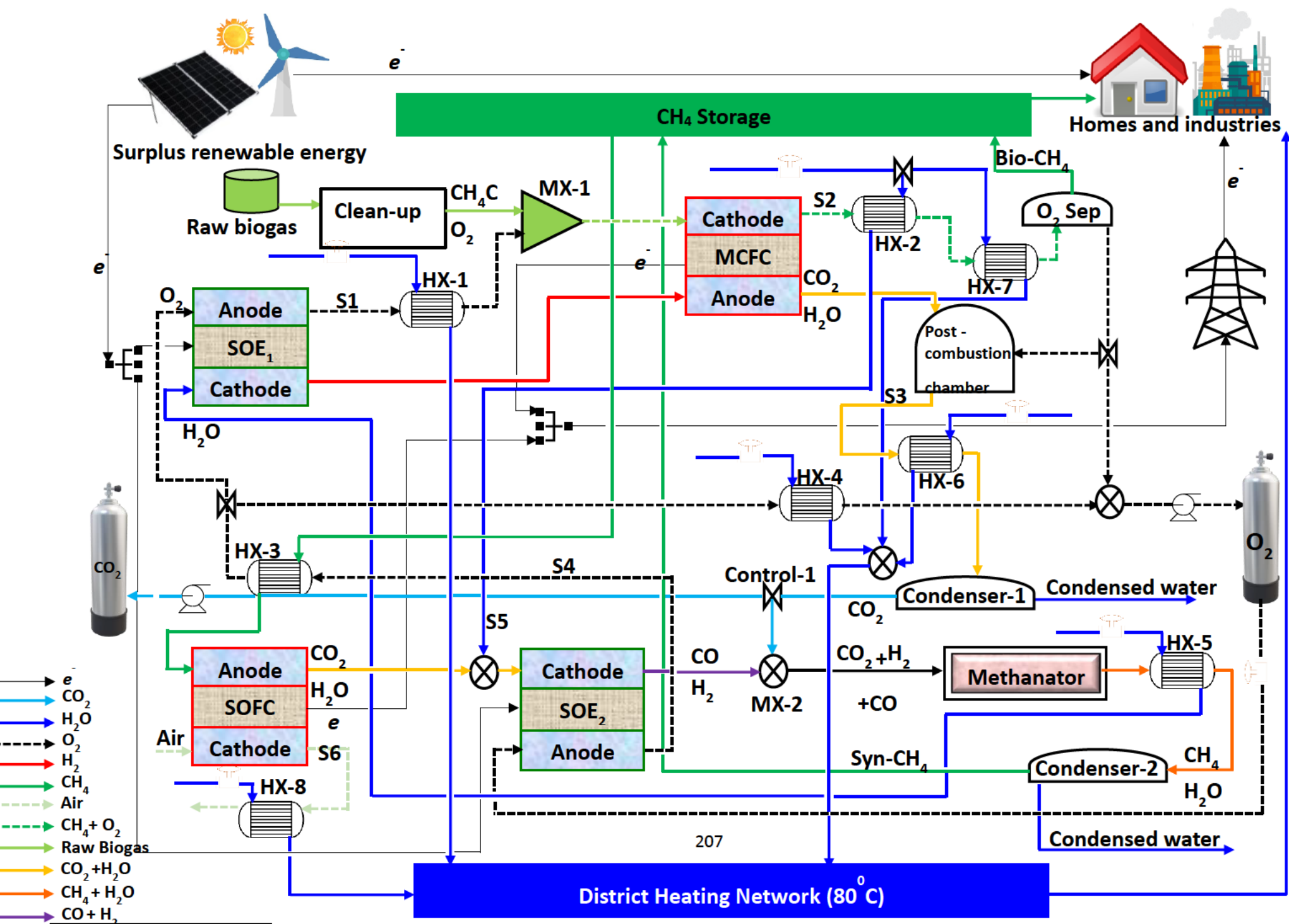


Figure 9.1: The Proposed integrated power-2-gas energy and decarbonisation system

9.2.2.1 Methanation Reactor

Methanation involves a chemical process where carbon dioxide and/or carbon monoxide are transformed into methane through the Sabatier reaction. The ample availability of low-cost natural gas historically led to a lack of large-scale methane production through this method. In recent times, the relevance of methane synthesis methods has escalated, driven by a shift in worldwide energy and environmental strategies, as well as the necessity for effective carbon dioxide use and the storage of extra renewable energy.

The methanation reaction is simply the hydrogenation of carbon monoxide and/or carbon dioxide, which occurs under moderate temperatures and pressures with the aid of metallic catalysts, resulting in the formation of CH₄ and H₂O as shown in Equations (9.1) and (9.2) (25).



The Methanation is an exothermic reaction (56) with the reactor temperature ranging from 503 to 1023K and the process pressures ranging from 4.4 to 84 atm (63). As already mentioned in Chapter 1, the important criteria for designing an efficient methanation plant include: (i) Operating under conditions that facilitate high methane yield and fast kinetics (i.e. low temperature and high pressure), (ii) Avoiding catalyst deactivation caused by sulphur poisoning, (iii) Preventing conditions such as extremely low temperatures or inadequate H₂:CO and or H₂:CO₂ ratios, which can lead to catalyst deactivation through the deposition of carbon and the formation of Nickel tetracarbonyl (Ni(CO)₄), and (iv) Preventing the sintering of catalysts at high temperatures (64).

Given the exothermic nature of the methanation reaction, achieving the desired temperature conditions in practice can be challenging (64). However, the presence of steam in the feed as it is the exit stream of SOE₂ in the integration plant proposed in this study can enhance the

hydrogen and oxygen content in the feed syngas, effectively reducing the likelihood of carbon deposition.

9.2.3 Model flowsheet

Figure 9.1 presents the integrated model flowsheet including all the subsystem units that have been modelled and presented in this thesis. This includes the solid oxide electrolyser (SOE₁) for steam electrolysis (Chapter 4), the MCFC (Chapter 5), the SOFC (Chapter 7), and the solid oxide electrolyser for co-electrolysis of CO₂/H₂O, denoted as SOE₂ (Chapter 8).

As shown in **Figure 9.1**, the SOEs receive their electrical energy (e^-) from an excess supply of renewable sources, and their thermal energy demand from integration with fuel cells. This setup enables SOE₁ to deliver H₂ to the MCFC anode inlet and SOE₂ to supply syngas to the methanation reactor. The hot exit stream from the SOE₁ anode, denoted as 'S1' and consisting of pure O₂, is cooled before being sent to a mixer (MX-1). Here, it combines with raw biogas (comprising CH₄ and CO₂), with its heat already extracted through heat exchanger 'HX-1' to produce hot water at 80°C for the district heating network. Cooling is essential to prevent potential combustion reactions between CH₄ and O₂, which can occur spontaneously at high temperatures, typically above 600°C. Consequently, the MCFC's operating temperature is maintained at 575°C for safety reasons mentioned earlier. The resultant mixture from the MCFC cathode outlet, 'S2,' is then cooled through heat exchangers 'HX-2' and 'HX-7' before undergoing oxygen separation ('O₂ Sep'). The purified oxygen obtained is then compressed and stored, while the remaining mixture, essentially upgraded biogas or biomethane 'Bio-CH₄' with very low CO₂ concentration, is injected into the natural gas grid, as depicted in **Figure 9.1**. 'HX-2' provides steam to the SOE₂ for co-electrolysis, and 'HX-7' supplies hot water to the district heating network at 80°C.

As mentioned in the preceding section, the exit stream of the MCFC anode, consisting of 'CO₂, H₂O, and unreacted H₂ and CO' undergoes complete combustion in a post-combustion chamber. This process converts any unreacted H₂ and CO into H₂O and CO₂. The resulting hot stream, 'S3,' is then cooled through heat exchangers 'HX-6' before it undergoes condensation in 'Condenser-1'. The condensed water produced can be stored and reused in the SOEs, while a fraction of the CO₂ is directed to a mixer 'MX-2' and the remaining is then bottled to be sold. This mixer combines it with syngas to be delivered to the methanation reactor for synthetic natural gas production.

The flow rate of CO₂ addition into the syngas is controlled using 'Control-1' to maintain a H₂/CO₂ ratio of 4:1, while also maintaining a H₂/CO ratio of 3:1 in the resulting mixture. Consequently, this leads to an average H₂/(CO+CO₂) ratio of 3.5:1. The SOFC is supplied with methane gas from the CH₄ storage, which is preheated through heat exchanger 'HX-3'. This heat exchanger 'HX-3' draws heat from the hot O₂ stream 'S4' from the SOE₂ anode outlet. The remaining thermal energy in the O₂ stream is further harnessed by heat exchanger 'HX-4', to produce additional heating for domestic use. The SOFC outlet stream, containing CO₂, H₂O, and unreacted H₂ and CO, is mixed with additional steam 'S5' before being delivered to SOE₂ for the production of syngas. This additional steam is added, and its flow rate is adjusted to ensure a sufficient supply of H₂ molecules, maintaining an optimal H₂/(CO+CO₂) ratio of 3.5:1 for efficient methane production in the methanation reactor. The hot exit stream from the methanator, containing CH₄ and H₂O, is first cooled by extracting its heat to generate steam for SOE1 through heat exchanger 'HX-5'. The resulting cooled gas is then passed through 'Condenser-2' to condense the H₂O, before the methane gas 'Syn-CH₄' is delivered to the storage. Air is supplied to the SOFC cathode, and the resultant hot exit stream 'S6' is used to produce additional heating for domestic use. The electricity produced by the MCFC and SOFC is transmitted to the power grid for distribution to homes and industries.

9.3 Evaluation of Thermodynamic Performance

To assess the thermodynamic efficiency of the proposed integrated power-to-gas and decarbonisation system, the system's energy, and exergy efficiencies, which correspond to the first and second laws of thermodynamics, were calculated. The steam electrolysis unit (SOE₁) is based on the design, constant input parameters, and simulations presented in Chapter 4 of this thesis. Similarly, the integration includes the design, constant input parameters, and the simulation of the MCFC from Chapter 5. The design, simulation, and input parameters of the SOFC unit are referenced from Chapter 7. Lastly, the co-electrolysis unit (SOE₂) is based on the design, constant input parameters, and simulation detailed in Chapter 8 of this thesis. **Table 9.1** provides a list of all input parameters assumed for the study of the overall performance of the plant.

Table 9.1: Technical specifications and operating parameters of the integrated energy System Components

Unit	Parameter	Values	Units
SOE ₁ input	Input H ₂ O flow rate	0.03	kgs ⁻¹
	Input H ₂ O temperature	25.0	°C
	Input H ₂ O Pressure	1.013	bar
	Operating temperature	900	°C
	Operating pressure	1.013	bar
	Sweep gas (O ₂) flow rate	0.01	kgs ⁻¹
	Sweep gas temperature	25.0	°C
	Sweep gas pressure	1.013	bar
	Steam utilisation factor	0.85	
MCFC input	Input biogas flow rate (CH ₄ -0.6, CO ₂ -0.4)	0.10	kgs ⁻¹
	Input biogas temperature	25.0	°C
	Input biogas Pressure	1.013	bar
	Operating temperature	575	°C
	Operating pressure	1.013	bar
	Fuel utilisation factor	0.85	
	O ₂ utilisation factor	0.20	
	CO ₂ utilisation factor	0.85	
SOFC input	Input fuel flow rate (CH ₄)	0.0045	kgs ⁻¹
	Input fuel temperature	35.00	°C
	Input fuel Pressure	1.013	bar
	O ₂ utilisation factor	0.20	
	Fuel utilisation factor	0.85	
	Operating temperature	910.0	°C
	Operating pressure	1.013	bar
SOE ₂ input	Operating temperature	1050	°C
	Operating pressure	1.013	bar
	Additional H ₂ O Input flow rate	0.06	kgs ⁻¹
	Additional H ₂ O Input temperature	25.0	°C
	Additional H ₂ O Input Pressure	1.013	bar
	Steam utilisation factor	0.85	
Methanation	CO ₂ utilisation factor	0.30	
	Operating temperature	229.85	°C
Unit	Operating pressure	4.458	bar

9.3.1 Energy Efficiency

The calculation of energy efficiency begins with determining the overall energy input. There are two sources of energy input (EI_{Total}) for the system: methane gas from the storage, as shown in **Figure 9.1** and the electricity supplied to the SOEs from a renewable source as outlined in Equation (9.2). The raw biogas input serves solely as a source of CO₂ into the system, which in turn, is then upgraded into biomethane for potential injection into the national natural gas grid or CH₄ storage.

$$EI_{Total} = (M_{NG} \times LHV_{NG}) + P_{Elect-SOE} \quad (9.3)$$

where M_{NG} denotes the molar flow (mols⁻¹) of the natural gas supplied, LHV_{NG} denotes the lower heating value (Jmol⁻¹) of the natural gas and the $P_{Elect-SOE}$ is the electricity supplied to the SOEs.

In the proposed integrated power-to-gas and decarbonisation system, electricity, thermal energy, methane, O₂, and CO₂ are produced as various outputs. The total net output of electricity ($P_{Elect-Net}$) is calculated using Equation (9.4) as follows:

$$P_{Elect-Net} = P_{Elect-MCFC} + P_{Elect-SOFC} - P_{Elect-Misc} \quad (9.4)$$

where $P_{Elect-MCFC}$ and $P_{Elect-SOFC}$ denote electricity generated by the MCFC and the SOFC, respectively, while $P_{Elect-Misc}$ refers to the aggregate of miscellaneous electrical consumption within the integrated system. The miscellaneous electrical consumption includes all electricity used by the condensers and the pump for membrane separation.

Thermal energy generated by the integrated system includes heat from the MCFC, SOFC, hot exit streams from all units, the methanation unit, and heat from the SOEs. However, a portion of the heat from the hot exit streams of all units is utilised as a heat source for other components or units within the system, as illustrated in the **Figure 9.1**. This is achieved either through heat exchangers or by directly mixing with the fresh input stream. The remaining surplus heat is

used to produce hot water at 80°C for the domestic district heating network, which accounts for 6.9% of the total heat generated by the integrated system. The overall heat ($Q_{TH-Total}$) generated by the integrated PTG and decarbonisation system is determined from Equation (9.5)

$$Q_{TH-Total} = Q_{TH-Fuel\ cell} + \Delta Q_{TH-SOEs} + Q_{TH-Methanation\ plant} + \Delta Q_{TH-District\ heating} \quad (9.5)$$

where $Q_{TH-Fuel\ cell}$ denotes the heat generated by the two fuel cells, $\Delta Q_{TH-SOEs}$ denotes the net heat released by the SOEs after meeting their internal heating demand, $Q_{TH-Methanation\ plant}$ indicates the heat released by the methanation plant, and $\Delta Q_{TH-District\ heating}$ represent the surplus heat extracted from the hot exit streams of the integrated system, which is used for producing hot water at 80°C for domestic district heating network.

The energy content of the methane produced (E_{CH_4}) can be determined from Equation (9.6) as follows:

$$E_{CH_4} = M_{CH_4} \times LHV_{CH_4} \quad (9.6)$$

where M_{CH_4} is the molar flow (mols⁻¹) of the produced methane gas, and LHV_{CH_4} denotes the lower heating value (Jmol⁻¹) of the methane gas.

Lastly, the energy associated with the CO₂ produced ($E_{CO_2-produced}$) in kW by the integrated system for potential industrial use is estimated by considering the average energy requirement ($E_{avg-CO_2-captured}$) for the commonly used reboiler heat duty in an amine CO₂ capture plant, as reported in the literature (351–355). This varies from 3.7 to 5.80 GJ/Ton of CO₂ and is calculated using Equation (9.7).

$$E_{CO_2-produced} = E_{avg-CO_2-captured} \times \dot{m}_{CO_2-produced} \quad (9.7)$$

where $E_{avg-CO_2-captured}$ represent the average energy requirement ($4.75 \text{ GJTon}^{-1} \text{ CO}_2$ captured) and $\dot{m}_{CO_2-produced}$ denotes the mass flow rate of the produced CO_2 (kgs^{-1}).

Production of oxygen by the SOE units are not associated with any energy output. Therefore, the first law of thermodynamic efficiency ($\eta_{1^{st}law}$) for the proposed integrated power-to-gas and decarbonisation system is calculated using Equation (9.8), as shown below:

$$\eta_{1^{st}law} = \frac{P_{Elect-Net} + Q_{TH-Total} + E_{CH_4} + E_{CO_2-produced}}{EI_{Total}} \quad (9.8)$$

9.3.2 Exergy Efficiency

For the analysis of the integrated system according to the second law of thermodynamics, similar to the first law, the total exergy input is initially calculated using the specific exergy of the fuel. Differing from energy, which is conserved, exergy is the maximal work potential of a system's matter, workflow or thermal energy as it stabilises with an environment at a reference temperature ($T_{ambient}$) and pressure ($P_{ambient}$) (356). However, in practical applications, exergy diminishes or gets destroyed due to imperfections and irreversible changes in processes.

The system has two sources of exergy input: the exergy from input methane gas from the storage and the exergy from direct electricity, which is sourced from renewable energy. The overall exergy input ($\psi_{Total input}$) (kW) for the integrated system is determined using Equation (9.9).

$$\psi_{Total input} = \left(\dot{m}_{CH_4} \times \psi_{CH_4}^0 \times \frac{1}{molar\ mass_{CH_4}} \right) + P_{Elect-SOE} \quad (9.9)$$

where $\dot{m}_{CH_4}$ represent the mass flow rate of the methane gas (kgs^{-1}), $\psi_{CH_4}^0$ denotes the specific exergy of the methane gas (kJmol^{-1}) and $molar\ mass_{NG}$ represents the molar mass of the methane gas (kgmol^{-1}).

The proposed system's output exergies include the electricity output of the fuel cells, the exergy of the integrated system-generated heat, the exergy of the produced methane, the combined exergy of the oxygen from the two SOE units, and the exergy of the excess CO₂ produced by the integrated system. The total exergy of the thermal energy generated ($\psi_{TH-Total}$) by the integrated system is the sum of individual exergies of the heat generated from each unit, as detailed in Equations (9.10) and (9.11) below (357):

$$\psi_{TH-Total} = \sum \psi_{TH-i} + \sum \Delta\psi_{TH-j} \quad (9.10)$$

where ψ_{TH-i} denotes the heat exergies from the i^{th} unit (where 'i' denotes a fuel cell or methanation plant), and $\Delta\psi_{TH-j}$ indicates the resultant exergies from the j^{th} unit (where 'j' refers to SOEs or District heating), with

$$\psi_{TH-k} = Q_{TH-k} \left(1 - \frac{T_{ambient}}{T_k} \right) \quad (9.11)$$

where $k = i$ or j

The calculations of the exergy values (ψ_α) for methane, oxygen, and CO₂ are based on their individual specific exergy values (obtained from (197)) as shown in Equation (9.12).

$$\psi_\alpha = \dot{m}_\alpha \cdot (\psi_\alpha^0) \cdot \frac{1}{(Molar\ mass)_\alpha} \quad (9.12)$$

where $\dot{m}_\alpha$ represent the mass flow rate of α (kgs⁻¹) (where α represents methane, oxygen and CO₂), ψ_α^0 denotes the specific exergy of α (kJmol⁻¹) and $Molar\ mass_\alpha$ represents the molar mass of α (kgmol⁻¹).

Conclusively, the efficiency of the proposed integrated PTG and decarbonisation system, according to the second law of thermodynamics ($\eta_{2^{nd}law}$), can be determined using Equation (9.13) below:

$$\eta_{2^{nd}law} = \frac{\psi_{TH-Total} + \psi_{\alpha} + P_{Elect-Net}}{\psi_{Total\ input}} \quad (9.13)$$

Figure 9.2 illustrates the detailed influx and outflux, and the total exergy balance of the combined PTG and decarbonisation system, **Table 9.2** provides an overview of the proposed plant's thermodynamic efficiency.

Table 9.2: Thermodynamic assessment of the proposed integrated system.

Parameter	Flow rate (kg/s)	Power (kW)
Methane gas Input	0.004	223.0
Electricity Input to SOE1		333.2
Electricity Input to SOE2		2122
Electricity Output of MCFC		221.5
Electricity Output of SOFC		162.2
Thermal energy output MCFC		191.6
Thermal energy output SOFC		142.9
Thermal energy output SOE1		-123.9
Thermal energy output SOE2		430.4
District heating		146.3
Methanation plant		217.6
Methane produced	0.011	560.1
CO ₂ output	0.039	185.0
Net O ₂ Output	0.097	
Miscellaneous		0.209
Hot water produced at 80°C	0.587	
Distilled water	0.030	
Biomethane production rate	0.047	2114
Energy efficiency (%)	79.7	
Exergy efficiency (%)	55.5	

*Negative sign means energy consumption

The **Table 9.2** and **Figure 9.2** provide a comprehensive overview of the operational dynamics and efficiency of the proposed integrated PTG energy and decarbonisation system.

The system reveals that a significant 91.4% of the exergy input, as depicted in **Figure 9.2**, originates from electrical energy of which 86.4% of the energy input is consumed by the SOE₂. This is primarily utilised for the SOE₁ and SOE₂ units, which are crucial for hydrogen and

syngas production. The methane gas input, contributing to only 8.6% of the exergy input, plays an essential role in the operation of the SOFC.

The electrical outputs from the MCFC and SOFC, which are 221.5 kW and 162.2 kW respectively as indicated in **Table 9.2**, constitute approximately 14.3% of the system's total exergy output, as shown in **Figure 9.2**. The net thermal energy generated by the system, amounting to 1005 kW, contributes only 19.4% to the system's total exergy output.

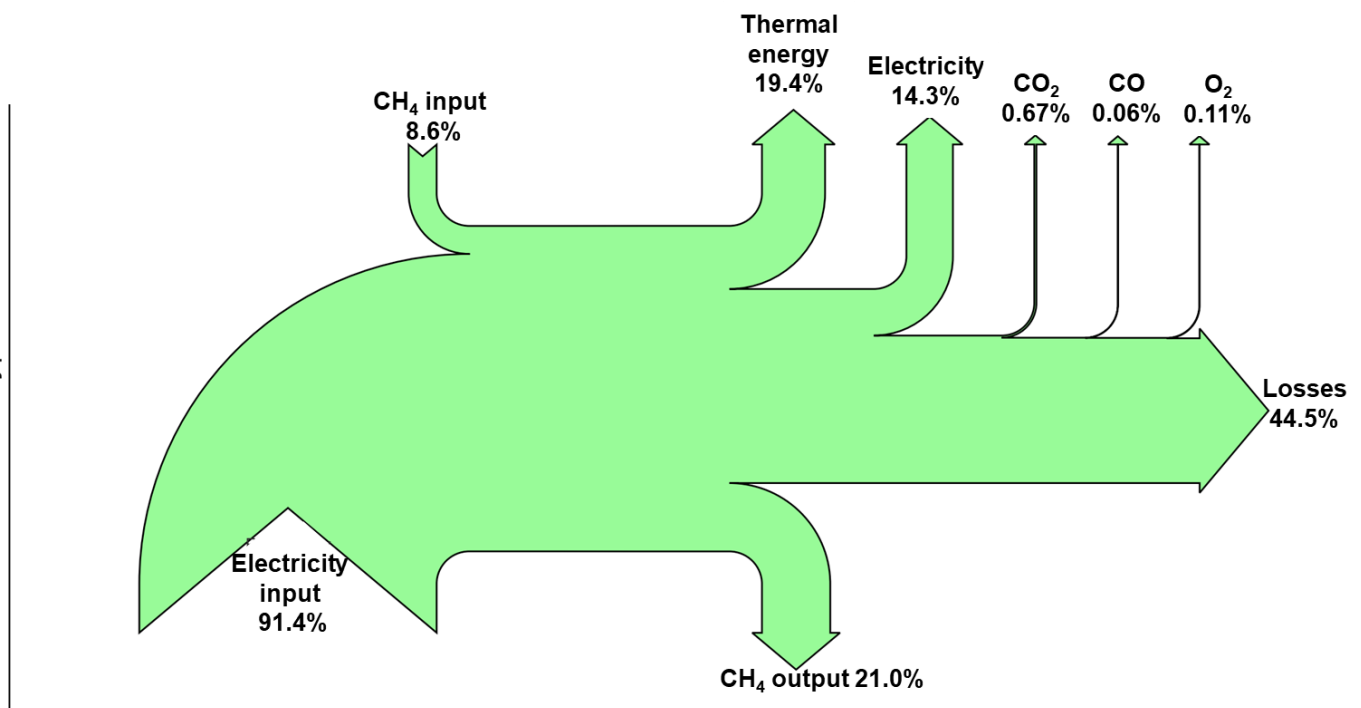


Figure 9.2: Sankey diagram representing exergy flow in the system

In terms of product generation, the system produces methane at a rate of 0.011 kg/s, biomethane at 0.047 kg/s, and CO₂ at 0.039 kg/s. Additionally, 146.3 kW of thermal energy, extracted from the hot exit streams within the integrated system, is channelled into the district heating network.

This points to a strong alignment with decarbonisation goals, as it leverages CO₂ for beneficial use.

The energy efficiency of the system is at 79.7%, indicating effective conversion of input energies into useful outputs. However, the exergy efficiency, at 55.5%, suggests that there is room for improvement in maximising the work potential of the energy inputs.

9.4 Techno-Economic analysis of the proposed integrated energy system

This section explores the financial viability and strategic investment plan necessary for the successful implementation and operation of the plant.

Central to this analysis is **Table 9.3**, which presents a list of the capital costs associated with each part of the equipment and selling prices of energy and by-products.

The total capital expenditure CAPEX, a critical indicator in any project assessment, represents the cumulative investment required to bring the system to operational status. This is determined as the sum of the costs of all system components, Using Equation (9.14) below:

$$CAPEX = \sum_i (Cost\ of\ Capital\ Component)_i \quad (9.14)$$

A discount rate of 3% (358) is applied. It is projected that the annual costs for operation and maintenance will amount to 2.5% of the initial capital expenditure (190). Additionally, regular replacement parts of SOEs, MCFC, SOFC, and other units are necessary, with the annual expenses for these replacements estimated at 5% of the initial investment (190). The system's total annual cost ($COST_t$) comprises the sum of its annual capital ($CAPEX_t$), operational ($OPEX_t$), fuel ($NGEX_t$), and, replacement ($REPEX_t$) expenditure as detailed in Equation (9.15) (359):

$$COST_t = \frac{CAPEX_t}{(1+r)^t} + OPEX_t + NGEX_t + REPEX_t \quad (9.15)$$

Where t denotes the number of years of operation, and r represent the discount rate.

Table 9.3: Capital expenditures and selling Prices of energy technologies and by-products.

Unit/Technology	Value	Unit	Reference
SOE	381	£/kWe	(293)
MCFC	2372	£/kWe	(292)
SOFC	712	£/kWe	(360)
Methanation plant	1704	£/kg	(361)
Miscellaneous (i.e. Heat exchanger, piping)	159.1	£/kWe	(362)
Amine based CO ₂ capture	1.46	£/kg	(363)
Cost of Renewable electricity for SOEs	35.3	£MWh	(358)
Selling price of electricity	0.1514	£/kWh	(364)
District heating network	624	£/MWh	(365)
Selling price of Methane & Biomethane	1.06	£/kg	(366)
Selling price of Oxygen	0.068	£/kg	(367)
Selling price of distilled water	1.5	£/kg	(368)
Selling price of carbon dioxide	0.038	£/kg	(367)

9.4.1 Levelised cost of energy (LCOE)

The levelised cost of energy (LCOE) represents the average energy cost over the plant operation, offering insight into the cost per unit of energy generated by the system over its lifetime or period of interest. The LCOE of the integrated system can be calculated using Equation (9.16) as follows:

$$LCOE = \frac{COST_t}{Energy\ Produced_{Total}} \quad (9.16)$$

where $COST_t$ is expressed in £, and total energy produced ($Energy\ Produced_{Total}$) is measured kWh.

The LCOE of £72.2 per MWh obtained in this study, as shown in **Table 9.4**, positions it uniquely in the landscape of renewable energy technologies. Despite appearing high at first

glance, this LCOE is competitive within the renewable energy sector, particularly when the broader context of decarbonisation benefits are considered.

Comparatively, the **Table 9.4** shows LCOE values for various systems, ranging from traditional coal-fired power plants integrated with carbon capture technology like CLC (Calcium Looping Combustion) to advanced configurations like SOFC-GT (Solid Oxide Fuel Cell-Gas Turbine) hybrids. Notably, the range of LCOE for these systems varies widely, from as low as £40.82 per MWh in the case of IGFC (Integrated Gasification Fuel Cell) systems to higher ranges exceeding £100 per MWh for some coal-fired systems with advanced carbon capture.

The LCOE of £72.2 per MWh for this study, while higher than some traditional and hybrid systems, falls within a reasonable range for renewable energy projects that often prioritise environmental benefits alongside economic viability. It is also indicated from **Table 9.4** that the thermodynamic efficiency of the proposed integrated energy system surpasses some of other systems. This suggests that the energy being produced by this system is not only cost-effective but also aligns well with sustainability goals.

Figure 9.3 illustrate the breakdown of different cost components contributing to the LCOE.

Table 9.4: Comparative analysis of this study's techno-economic performance against other energy systems in the literature

System's Configuration	Outputs	Energy / Exergy Efficiency	LCOE (£/MWh)	Ref
SOFC-based IGFC power plant	Electricity	49.4% HHV	69.14	(79)
SOFC-GT hybrid power plant	Electricity	41.6%	64.42	(369)
IGFC	Electricity	58%	40.82	(80)
Combined cycle using NG integrated with MCFC	Electricity	57.53%	46.2	(370)
Coal-fired power plant integrated with CLC	Electricity		81.2- 103.9	(371)
MCFC-NGCC integrated	Electricity	57.5%	70.66	(190)
Coal fired plant integrated with MCFC	Electricity	-	64.73	(193)
Coal fired plant integrated with MCFC	Electricity	47.3%	81.98	(195)
SOFC-GT integrated ORC plant	Electricity	49.29%	51.63	(372)
NGCC-MCFC	Electricity	52.5% HHV	62.68	(192)
MCFC-electrochemical cycle - alkaline electrolyser-Thermo- PV	Heating, electricity, cooling and H ₂	86.8% / **80.4%	-	(373)
SOFC-GT-CLC powered by diesel	Heating, electricity, and cooling	54.1% / **52.3%	-	(374)
Offshore wind round 3	Electricity		106	(375)
Large scale PV	Electricity		67	(375)
Onshore wind 5MW UK	Electricity		63	(375)
Biomass conversion	Electricity		87	(375)
This work	Electricity, heating, O ₂ , CO ₂ , CH ₄ , Biomethane and distilled water	79.7% / **55.5%	72.2	-

Exergy**

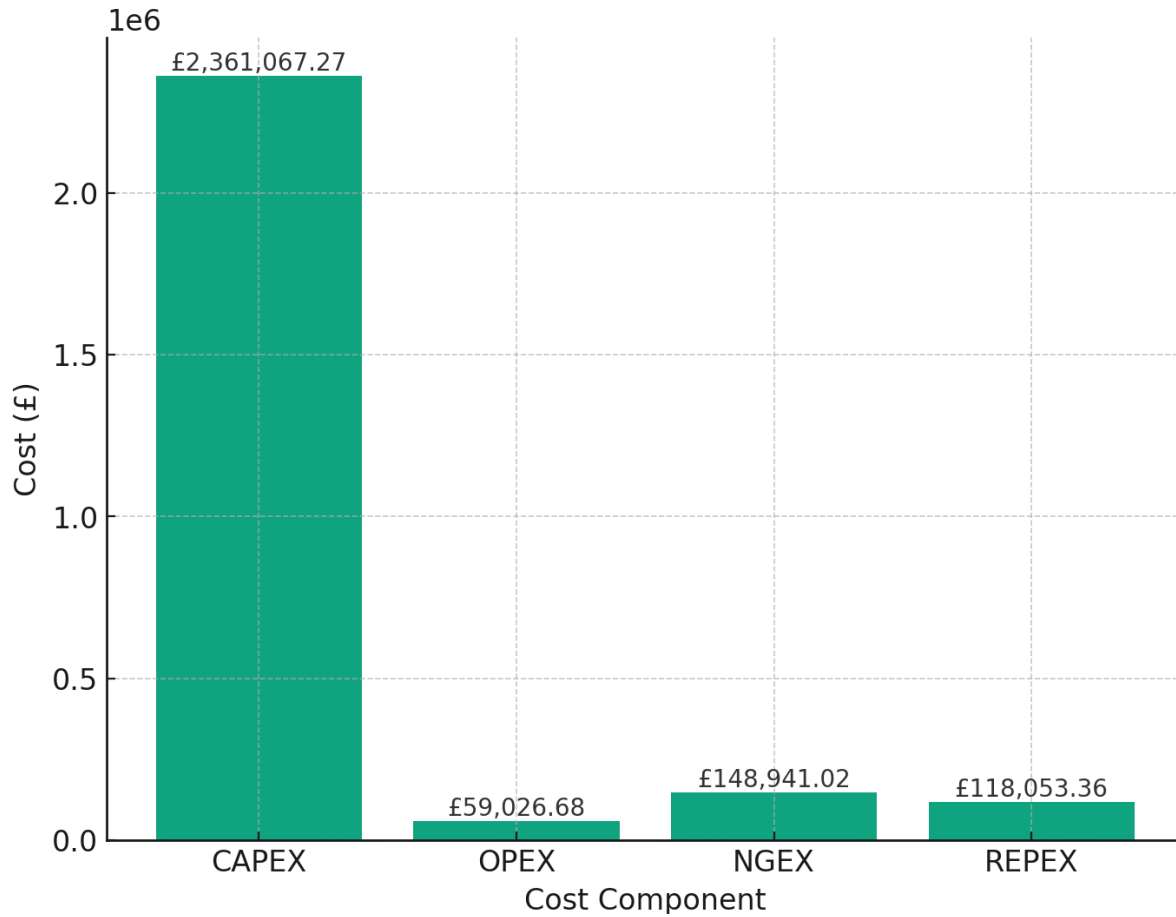


Figure 9.3: The breakdown of different cost components contributing to the LCOE

9.4.2 Payback Period

The simple payback period is a metric in assessing the financial viability of any energy project. It is determined using Equation (9.17), the payback period provides a straightforward understanding of the time required for the initial investment to be recovered through the net profits generated by the system.

$$\text{Payback period} = \frac{\text{CAPEX}}{\text{Total Revenue}_{\text{Annual}} - \text{Total Cost}_{\text{Annual}}} \quad (9.17)$$

Figure 9.4 presents the Financial Break-Even analysis using the simple method, showing the cumulative net income revenue and costs over a period of 7 years.

The obtained payback period of 2.92 years, as observed in the study, is notably reasonable. This duration is relatively short for energy projects, which typically expect returns over longer

periods. A payback period under three years suggests that the integrated energy system is not only financially viable but also efficient in terms of investment recovery.

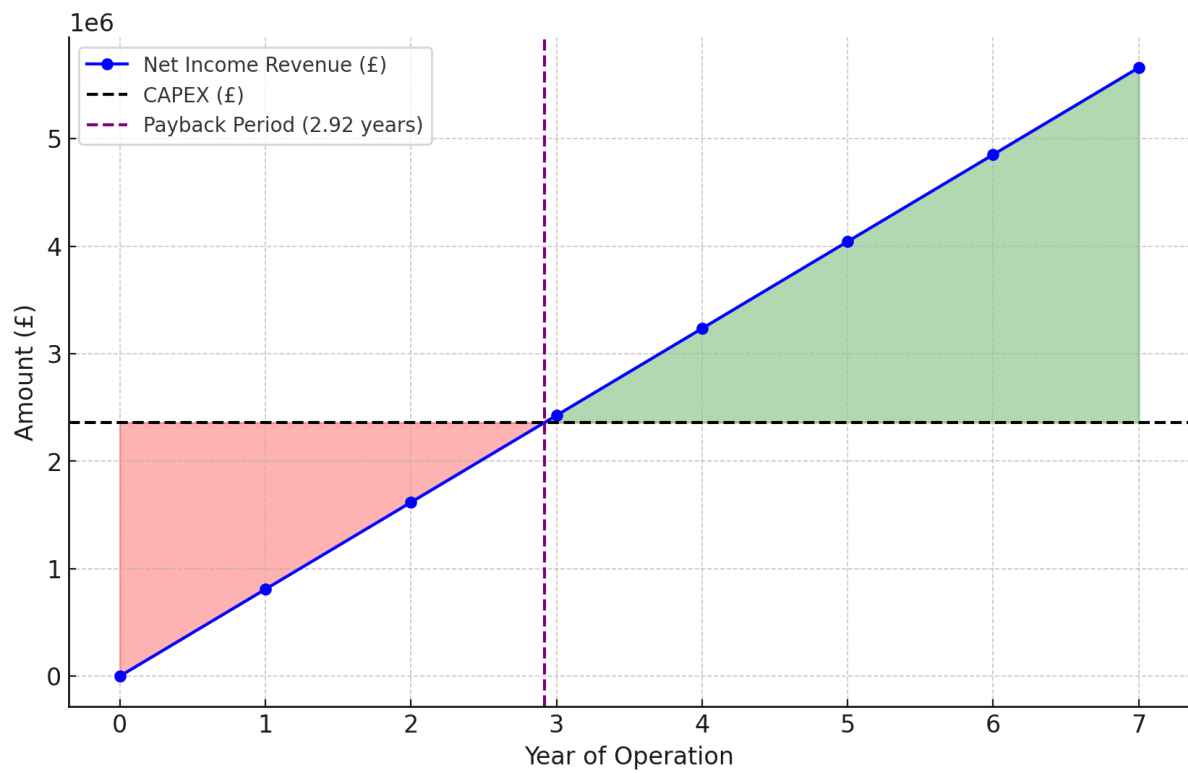


Figure 9.4: Financial break-even analysis using a simple method to estimate the payback period

CHAPTER 10: CONCLUSION AND OUTLOOK

10.1 Introduction

The primary goals and objectives outlined in chapter 1 have been successfully met. Consequently, it can be concluded that the research endeavour was effective. This chapter offers a recapitulation of the key conclusions derived from the analyses conducted in the thesis. It starts by delineating the principal outcomes of each study in the respective chapters. Subsequently, it highlights potential directions for future research in this field.

10.2 Conclusion

10.2.1 Chapter 2

The escalating energy demands associated with conventional CO₂ capture technologies have undeniably been a pivotal trigger for this research. Conventional methods, while effective in reducing carbon emissions, impose a significant energy penalty, thus heightening the Levelised Cost of Electricity (LCOE). This has prompted a search for more sustainable and energy-efficient solutions.

Molten Carbonate Fuel Cells (MCFCs) emerged as a dual solution, a revolutionary technology. This dual capability presents a groundbreaking approach to addressing the challenges of energy demand in CO₂ capture technologies.

The studies reviewed in this section underscore the potential and advantage of integrating MCFCs with various power generation technologies over other CO₂ capture technologies. Such integrations have shown promising results in improving overall plant efficiencies and reducing carbon emissions. For instance, the integration of MCFCs with natural gas combined cycles (NGCCs) and internal combustion engines has demonstrated substantial reductions in CO₂ emissions, with a minimal impact on the electrical efficiency of the systems.

Further research and development in MCFC technology, focusing on enhancing its efficiency and cost-effectiveness, could pave the way for its widespread adoption in power plants and other large industrial facilities. Additionally, the integration of MCFCs with other emerging CO₂ capture technologies, like cryogenic capture or oxygen ion transfer membranes, could further optimise the overall efficiency of these systems.

10.2.2 Chapter 3:

Throughout this methodology chapter, a comprehensive overview of the techniques used to model and simulate the operation of MCFC, SOFC, and SOE has been provided. The study utilised Aspen Plus™, integrated with spreadsheet tools, to effectively simulate complex electrochemical reactions and thermodynamic processes, incorporating custom-built models to account for electrochemical behaviours not natively supported by Aspen Plus.

Key assumptions and limitations underlying these models were also presented, including steady-state operations, ideal gas law assumptions, and the simplifications made for pressure drops and ion movement. Despite these inherent simplifications, the models offer valuable insights into the thermodynamic and electrochemical dynamics of these systems, while also providing a flexible and powerful approach for optimising performance through sensitivity and exergy analyses. These models serve as effective tools for both the preliminary design and techno-economic evaluation of the integrated power-to-gas system.

10.2.3 Chapter 4:

In chapter 4, an Aspen Plus model was developed to investigate the electrolysis of steam in an SOE. The incorporation of both proposed and established mathematical models for electrochemical reactions and thermal energy requirements has enhanced our understanding of the system's electrochemical reactions, thermodynamics, and heat transfer. The model's

validation against experimental data and subsequent simulation results have been instrumental in illustrating how various parameters such as operating temperature, steam utilisation factor, and current density influence SOE performance.

The employment of the Box-Behnken approach for optimising SOE performance and energy efficiency yielded significant findings. The optimised values for the total thermal energy demand, electrical energy demand, and total energy demand of the SOE were determined to be 68.1 ± 8.7 (kJ(molH₂)-1), 170.1 ± 14.6 (kJ(molH₂)-1), and 351.3 ± 3.9 (kJ(molH₂)-1) respectively. The study has provided an insight into enhancing SOE performance and energy efficiency, contributing significantly to the development of clean and sustainable energy systems.

10.2.4 Chapter 5:

Chapter 5 presents a system-level simulation model of MCFC stacks for the decarbonisation integrated plants project. The model, validated against experimental data, was used to carry out sensitivity analysis and lastly investigates the effects of oxidant composition on overall energy generation. The model incorporates electrochemical and mass balance aspects and considers various input parameters. The model outputs include current density, cell voltage, power generation, thermal energy release, oxidant flow rates, and outlet flow compositions.

The MCFC model accurately predicts I-V characteristics across different temperature and pressure conditions, with maximum relative errors consistently below 3% and high correlation coefficients above 0.994. The model performs better at higher temperatures (650 °C), with a maximum relative error of 0.9% at 3 atm operating pressure. This accuracy indicates the model's potential for guiding MCFC system design and operation.

The Sensitivity analyses performed using the model reveal that, fuel utilisation significantly influences MCFC performance. Based on how the recirculation of spent fuel is design in this

study, as fuel utilisation increases, cell voltage and power-to-heat ratio decline, while electricity output efficiency rises by approximately 65%.

10.2.5 Chapter 6

Chapter 6 introduces an innovative approach to biogas upgrading, designed to overcome the high energy demands and costs associated with current technologies. The proposed system, a coupling of an MCFC and an SOE, offers an energy-efficient decarbonisation process that can potentially reduce or even eliminate energy requirements. This solution not only adheres to quality standards for grid injection but also tackles the economic and technical challenges of integrating biogas into the grid, thereby making a substantial contribution to sustainable and clean energy production.

Utilising a system-level simulator of MCFC and SOE developed in previous studies chapter 4 and chapter 5, the study demonstrates that the CO₂ fraction in raw biogas significantly impacts the net thermal power output of the integrated SOE-MCFC system. A fuel utilisation factor of 0.85 in the MCFC is identified as critical for system viability, particularly in the biomethane industry, as it substantially increases the net thermal power output. The system achieves high CO₂ capture efficiency and notable net thermal power outputs, indicating an energy efficiency of 85.35%. However, a trade-off between the quality of raw biogas and the system's power output has been identified, necessitating strategic decision-making in practical applications. Despite high initial costs, the technology presents long-term cost-effectiveness, particularly due to its self-sustaining nature and capability to generate net system thermal power.

10.2.6 Chapter 7:

Chapter 7 presents a system-level simulation model of an SOFC stack, designed to integrate into power-to-gas and decarbonisation plant proposed as detailed in Chapter 1 of this thesis. The model incorporates both electrochemical and mass balance considerations and takes into

account various input parameters. Key model outputs include current density, cell voltage, and electrical power generation. The model was validated against three existing studies and demonstrated a high level of agreement, against the three. Overall, the model has proven to be both robust and reliable, with the highest standard deviation of 0.02 in the results obtained from the detailed flowsheet of the simulation when compared to study (311).

Furthermore, this study presents detailed investigation into the performance of the SOFC stack under various operating conditions, particularly focusing on the fuel utilisation factor (U_f), current density, and steam-to-carbon (S/C) ratio. The results reveal that a higher U_f leads to increased AC efficiency due to enhanced hydrogen consumption in electrochemical reactions. However, this also results in a slight decrease in cell voltage. Operating at an optimal current density range of 1690 to 1940 $\text{A}\cdot\text{m}^{-2}$ yields a balanced AC efficiency of 50.3–54.8%, a cell voltage of 0.68–0.71 V, and a power output of 110.0–119.7 kW.

On the other hand, elevated S/C ratios have a negative impact on both cell voltage and AC efficiency. The study recommends operating the SOFC stack at a relatively low S/C ratio to prevent carbon formation on the electrodes while maintaining high performance.

Ultimately, the findings provide key insights into the trade-offs between AC efficiency, cell voltage, and AC power.

10.2.7 Chapter 8:

Chapter 8 presents several key findings from the modelling and simulation of a SOE for the co-electrolysis of steam and CO_2 , aimed at producing syngas. These findings are intended to inform the design and optimisation of the proposed decarbonisation, and power-to-gas technology plant detailed in Chapter 1 of this thesis. The SOE model simulated in the study receives its inputs from the exit streams of the SOFC and, in turn, delivers its exit streams to the methanation unit for methane production, which is then sent to the national grid. The

integration of SOEs with various energy sources, as well as the interest also shown by the United States Department of Energy, underscores the potential of this technology in large-scale hydrogen production. Through comprehensive modelling and simulation efforts, this study has provided deep insights into the physical and chemical processes occurring within SOEs.

The study highlighted the complexities involved in the co-electrolysis process, especially when compared to individual electrolysis processes. It was found that the co-electrolysis of steam and carbon dioxide is not just a simple combination of two separate reactions but involves a complex interplay of various reactions, as indicated by the equations detailed in this chapter. This complexity demands an intricate understanding of the reaction mechanisms and the conditions that favour certain product formations over others.

The effects of operational parameters, such as temperature and pressure, were shown to significantly influence the performance of SOEs. Other operational parameters were not included in this chapter since similar results obtained for steam electrolysis, as presented in Chapter 4, were also observed. Higher operating pressures enhance gas-phase diffusion in the porous electrodes, improving the availability of steam and CO₂ at the reaction sites, and thereby increasing the cell voltage. Similarly, the impact of cell temperature on the composition of the cathode outlet stream was profound. An increase in operating temperature leads to a higher mole fraction of CO and lower H₂, attributed to the varying kinetics of steam electrolysis and the reverse water gas shift reaction.

Validation of the model with experimental data from other studies further strengthens the confidence in its predictive capabilities. The results align well with the existing literature, reinforcing the model's applicability in optimising the performance of SOEs for syngas production.

The chapter lays another groundwork for the proposed decarbonisation and power-to-gas technology plant. It highlights that the formation of CH_4 through reversed steam reforming (as illustrated in (8.2) and (8.4)) is generally not advantageous in the co-electrolysis process. Conversely, the reversible water gas shift reaction (WGSR) might play a significant role in CO production, subject to specific operating conditions. The insights gained here are instrumental in enhancing syngas production efficiency and effectiveness in the proposed power-to-gas plant.

10.2.8 Chapter 9:

As we move towards complete reliance on renewable energy sources, the role of carbon capture and utilisation becomes increasingly vital for reducing atmospheric CO_2 concentrations and achieving net zero CO_2 emissions, especially in the energy generation sector. This study introduces an integrated thermal and electrical energy system within a fuel-cell-based Power-to-Gas framework, focusing on generating and storing power, thermal energy, carbon dioxide, and oxygen. The system, comprising SOEs, MCFC, and SOFC, along with a methanation unit, is designed to optimise the use of surplus renewable electricity. This comprehensive assessment of the system, including economic, energy, and exergy factors, reveals a total electrical output of 383.7 kW and a net thermal output of 1005 kW. Additionally, the plant's production rates for methane, excess CO_2 , net oxygen, and biomethane, coupled with high energy and exergy efficiencies (79.7% and 55.5%, respectively), demonstrate the system's potential. The calculated LCOE at 72.2 £/MWh and a payback period of 2.92 years underscore the economic viability and sustainability of this integrated energy system. Its quick return on investment and efficient performance makes it an attractive option for investors and stakeholders seeking sustainable, economically feasible energy solutions.

10.3 Outlook

Looking ahead, there is an opportunity to enhance these models further. Future work should focus on integrating more comprehensive physical and chemical dynamics into the models. This will involve exploring ways to accurately simulate dynamic and non-ideal behaviours that are inherent in real-world systems.

The findings from chapter 4 open up avenues for future research, particularly in determining the most effective energy sources based on the user's target and the availability of different energy sources. Further investigation into the balance between electric, thermal, and waste stream sources could lead to more refined strategies to minimise the costlier energy inputs. This area of research holds significant potential for advancing the field of sustainable energy systems, offering opportunities to explore more efficient and cost-effective solutions.

Despite promising results for decarbonising the energy generation sector and district heating networks, challenges in commercialising cost-effective fuel cell technologies remain. Uncertainties in energy demand for homes, industries, and district heating, as well as the production of renewable green hydrogen, pose significant hurdles. To address these issues, further research is necessary to conduct in-depth analyses using real-world energy demand data from specific energy generation entities, councils, communities, or regions. Future studies should explore the feasibility of harnessing surplus thermal energy for enhanced power generation through integration with a steam turbine. The next step might also involve refining the system model across all sections. Experimental tests of the integrated system are also important to validate the model and to assess the effects of pollutants on cell performance and lifespan.

These investigations would help to improve understanding and implementation strategies for this innovative energy system.

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