CHAPTER 1

INTRODUCTION

The amount of energy consumption is an index of development of any country. The world energy demand has been increasing every year. The Fossil fuels are the main resources for the power generation for past few decades and are depleting from year to year. The \( \text{CO}_2 \) emissions are predominant during the power generation with fossil fuels. Emerging pace of Indian economic development need more energy and will influence the world energy system of their increasing share in the global fossil fuel trade and it will change the living standards for the crores of people. The need to use energy more efficiently has become a necessity since the large increases in oil prices in 1973 and increasing every year. The rises in the world market price of fuels, initiated by the oil crisis, has influenced the many nations to undertake a detailed appraisal of their indigenous reserves of fossil fuel and other resources.

The energy security and climate change are the global problems and need global solutions. So the challenge for all the countries is having a more secure, lower-carbon energy generation system, without effecting their economic and social development.

1.1 Energy Consumption :-

The distribution of energy resources throughout the world, although important, has not dictated patterns of consumption, since the major industrialized areas are concentrated in Western Europe,
the USA and JAPAN. Imported Oil and gas from Middle East and Africa have been major sources of fuel to these Nations. However, it seems certain that future patterns of fuel consumption will depend more on indigenous natural energy resources. Fuel usage throughout the world is affected by fuel availability, industrialization, transportation, economics and politics.

The utilization of energy (sector wise) throughout the world is given by: House hold 30%, Transportation (Rail: 6.8, Air 0.6, Road 9.6, Water 3%) : 20%, Agriculture:2%, Industry : 33% and electricity : 13% and Military : 2%. Interestingly less than one quarter of the world’s population consumes two thirds of the world’s energy i.e. USA using 33%. Western Europe almost 25% and Japan about 7%.

According to the world Energy outlook report 2007 [1], the facts about the World Energy Demands are

- As per the current policies of the government, the World’s Primary energy needs are expected to grow by 55% between 2005 and 2030. When compared to the present demand of 11.4 billion toe, it reaches to 17.7 billion toe. Around 50% of the increase in global demand goes to the power generation and 20% to meet the transport needs, particularly in the form of petroleum-based fuels.

- In the World’s final energy consumption, coal observers the biggest increase in demand from 25% in 2005 to 28% in 2030. About 80% of the increase in demand arises in India and China. The
requirement of natural gas increases moderately. The consumption of Electrical energy rising from 17% to 22%.

- To meet the expected global demand, about 22 trillion of investment is required in energy generation infrastructure. China alone requires to invest about $3.7 trillion – 17% of the total which is more than all other developing Asian countries. India needs to invest about $1.2 trillion, most of it is power sector.

- India and China alone account for 45% of the increase in global primary energy use, out of 74% share of developing countries.

- Increasing prices of oil and gas, are making coal to be more competitive fuel for base load power generation. About 45% of world coal usage is shared by India and China, which drive over 80% of the increase to 2030 in the Reference Scenario.

- Global primary energy demand increases by 1.3% per year over 2005-2030 which is 0.5% points less than in the Present Scenario. CO₂ emissions form energy generation stabilise in the 2020s and decreases by 19% in the year 2030, w.r.t. present status.

- Global primary energy demand increases to 6% in 2030 compared with the Reference Scenario (assuming that India and China economics grow as an average of 1.5% per year). In the IEO 2010[2] Reference case, the world marketed energy consumption increases by 49% from 2007 to 2035. Also the total energy demand in non-OCED (Organization for Economic Corporation and Development)
countries increases by 84% compared with an increase of 14% in OCED countries.

1.2 Indian Power Sector:

The power generation in India [3] as on 31-03-2011 has been presented as follows:

- **TotalInstalledCapacity**: 1,73,626.40 MW
- **StateSector**: 82452.58 MW (47.49%)
- **CentralSector**: 64412.63 MW (31.34%)
- **PrivateSector**: 36761.19 MW (21.17%)

The distribution of power generation on the basis of fuel used is given below:

- **TotalThermal** 112824.48 MW (64.98%)
  - Coal 93918.38 (54.09%)
  - Gas 17706.35 (10.2%)
  - Oil 1199.75 (0.69%)
- **Hydro (Renewable)** 37567.40 (21.64%)
- **Nuclear** 4780.00 MW (2.75%)
- **Renewal Energy Sources (MNRE)** 18454.52 MW (10.63%)

Renewable Energy sources include small hydro project, Biomass Gasifier, Biomass Power, Urban & Industrial waste power and wind energy.

India’s primary energy consumption per capita in 2007 was 0.53 toe per capita which is much lower than that of China (1.50
toe/cap) and also below the world average of 1.82 toe/cap. Per Capita power consumption in India was 543 kWh/cap (IEA 2009) which was only 20% of the world average of 2752 kWh/cap.

India has got very low CO₂ emissions per capita because of low energy consumption and high primary energy share of traditional biomass. India’s per capita emissions (1.19 tCO₂/cap) in 2007, were well below the world average emission of 4.38 tCO₂ / Capita.

In the world, the power sector is responsible for more than 41% of total energy related CO₂ emissions. In 2007, the power sector emitted about 12 gigatonnes (Gt) of CO₂ (IEA,2009), this figure climbs to 23 Gt of CO₂ by 2050. (IEA, 2010a), as per the IEA Baseline Scenario. This is due to the coal-fired power plant.

India is the 7th largest country in the world with the land area of 3.29 million square kilometers. India has the second largest population after China, according to the census 2011, with 1.21019 billion people, about 17% of the world’s total population. About 60% of the labour force involved in agriculture, 12% in industry and 28% in services in 2008.

India has the largest rural population in the world in 2008, 71% of the population (828 million people) lived in rural areas. About 2.3% of people had migrated to the urban areas, which is lower in India than many other developing countries (IEA,2010a) [1]. However there is a deficit of 9.8% in India to be electrified. [4]
India ranked 3rd in the world in 2007 in terms of absolute GDP, based on purchasing power parity, but it is in 100th position in terms of per-capita basis, well behind the other developing economics such as Brazil (69th), China (75th), Russia (54th) and South Africa (57th) [1]. There is a power deficit of 9.8% in India, which will be increased to 12.5% in the financial year 2011-12[4].

So India has set up a goal mission 2012 : power for all with following objectives:

- Sufficient power to achieve GDP growth rate of 8%
- Reliable and Quality power with optimum cost
- Commercial viability of power industry
- Power for all.

Considering the importance of power generation with lower emission to environment, in particular of CO₂ (the green house gas) and better cycle efficiency, we need better technology for long way.

The advanced Power Generation Technologies such as combined cycle power plant based on gas turbines, steam turbines, high temperature fuel cells are very much essential to meet the future demand.

1.3 Fuel Cells :-

Fuel cells are very important alternative for conventional power generation systems because of their low environmental effects and high efficiency. A fuel cell is an electrochemical reactor where the
chemical energy of fuel is directly converted into electricity and in some cases combined heat and power. A fuel cell consists of five parts, a cathode (positive electrode) and an anode (negative electrode) separated by an electrolyte and the electrical connector which connects the electrodes via an external load. The separator (bipolar) plate is the final component used for separating the fuel cells in a stack, simultaneously connecting the cells electrically in series. They are also distributing the fuel in the stack. The reactants, the oxidant and fuel, are continuously fed to the cathode and the anode respectively.

The fuel used depends on the type of the fuel cell and the oxidant is commonly oxygen in air. The electrochemical reaction takes place at the boundary of the three-phase zone where the electrode, the electrolyte and the gas interact.

A Fuel Cell can be considered as a “Cross-over of a heat engine and a battery. It is similar to a battery, its operation is based on electrochemical reaction. Fuel Cell resembles a heat engine because theoretically it can operates as long as the fuel is supplied to it. This combination provides both the advantages for fuel cells. In principle, a fuel cell resembles an instantly rechargeable battery. Mench [5] presented the difference between Fuel Cell and a battery based on the thermodynamic definition of a control volume and closed system. According to his perception, a fuel cell is a thermodynamically control
volume, fuel and oxidizer can flow across the system’s boundary where as a battery is a thermodynamically closed system.

The main advantages of fuel cell systems are:

- High efficiency
- Direct energy conversion (No combustor)
- Lower pollution
- No moving parts in the energy converter
- Fuel flexibility
- Hybrid systems and co-generation
- Easier carbon capture
- Scalability
- Quite operation
- Possibility of water production

1.4 Types of Fuel Cells

Fuel Cells can be classified based on the type of electrolyte, fuel and their operating temperature. This classification leads to:

1. Alkaline Fuel Cells (AFC)
   (a) Proton Ceramic Fuel Cell (PCFC)
   (b) Director Borohybride Fuel Cell (DBFC)
2. Proton Exchange Membrane Fuel Cell (PEMFC)
   (a) Direct Formic Acid Fuel Cell (DFAFC)
   (b) Direct Ethanol Fuel Cell (DEFC)
3. Direct Methanol Fuel Cell (DMFC)
4. Phosphoric Acid Fuel Cell (PAFC)
5. Molten Carbon Fuel Cell (MCFC)
6. Solid Oxide Fuel Cell (SOFC)

**Comparison of Fuel Cells**

The comparison of different fuel cells based on various parameters is shown in the Table 1.1

<table>
<thead>
<tr>
<th><strong>Table 1.1 Comparison of different types of fuel cells [6]</strong>:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameters</strong></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td><strong>Subtype</strong></td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
</tr>
<tr>
<td><strong>Operating Temperature (°C)</strong></td>
</tr>
<tr>
<td><strong>Charge carrier</strong></td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
</tr>
<tr>
<td><strong>Fuel</strong></td>
</tr>
<tr>
<td><strong>Oxidant</strong></td>
</tr>
<tr>
<td><strong>Product water management</strong></td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
</tr>
<tr>
<td><strong>Cogeneration</strong></td>
</tr>
<tr>
<td><strong>Reformer is required</strong></td>
</tr>
<tr>
<td><strong>Cell Voltage</strong></td>
</tr>
<tr>
<td><strong>Power density (kW/m$^3$)</strong></td>
</tr>
<tr>
<td><strong>Installation cost</strong></td>
</tr>
<tr>
<td>(UK $/kW)</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td></td>
</tr>
</tbody>
</table>

Contd......
<table>
<thead>
<tr>
<th>Parameters</th>
<th>High temperature</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Subtype</strong></td>
<td>MCFC</td>
<td>SOFC</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Lithium and potassium carbonate (LiAIO2)</td>
<td>Stabilized oxide electrolyte (Y₂O₃ ZrO₂)</td>
</tr>
<tr>
<td>Operating Temperature (°C)</td>
<td>~650</td>
<td>800-1000</td>
</tr>
<tr>
<td>Charge carrier</td>
<td>CO₃²⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Nickel</td>
<td>Perovskites</td>
</tr>
<tr>
<td>Fuel</td>
<td>H₂, CO, CH₄, other hydrocarbons</td>
<td>H₂, CO, CH₄, other hydrocarbons</td>
</tr>
<tr>
<td>Oxidant</td>
<td>O₂ in air</td>
<td>O₂ in air</td>
</tr>
<tr>
<td>Product water management</td>
<td>Gaseous product</td>
<td>Gaseous product</td>
</tr>
<tr>
<td>Product heat management</td>
<td>Internal reforming + Process gas</td>
<td>Internal reforming + Process gas</td>
</tr>
<tr>
<td>Efficiency</td>
<td>&gt;50%</td>
<td>&gt;50%</td>
</tr>
<tr>
<td>Cogeneration</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Reformer is required</td>
<td>Yes, Internal / External</td>
<td>Yes, Internal / External</td>
</tr>
<tr>
<td>Cell Voltage</td>
<td>0.7-1.0</td>
<td>0.8-1.0</td>
</tr>
<tr>
<td>Power density (kW/m³)</td>
<td>1.5-2.6</td>
<td>0.1-1.5</td>
</tr>
<tr>
<td>Installation cost (UK $/kW)</td>
<td>~2000-3000</td>
<td>3000</td>
</tr>
<tr>
<td>Capacity</td>
<td>155kW, 200kW, 250kW, 1MW, 2MW</td>
<td>1kW, 25kW, 5kW, 100kW, 250kW, 1.7MW</td>
</tr>
<tr>
<td>Applications</td>
<td>Transportations (e.g. marine-ships; naval vessels; rail); industries; utility power plants</td>
<td>Residential; utility power plants; commercial cogeneration; portable power</td>
</tr>
<tr>
<td>Advantages</td>
<td>High efficiency; no metal catalysts needed</td>
<td>Solid electrolyte; high efficiency; generate high grade waste heat</td>
</tr>
<tr>
<td>Drawbacks</td>
<td>High cost; corrosive liquid electrolyte; slow start up; intolerance to sulfur</td>
<td>High cost; slow start up; intolerance to sulfur</td>
</tr>
</tbody>
</table>
Table 1.2 Anode, Cathode and overall reactions for various fuel cells [7]

<table>
<thead>
<tr>
<th>Fuel Cell</th>
<th>Anode Reaction</th>
<th>Cathode Reaction</th>
<th>Overall Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEMFC</td>
<td>$H_2 \rightarrow 2H^+ + 2e^-$</td>
<td>$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$</td>
<td>$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$</td>
</tr>
<tr>
<td>AFC</td>
<td>$H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$</td>
<td>$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$</td>
<td>$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$</td>
</tr>
<tr>
<td>PCFC</td>
<td>$H_2 \rightarrow 2H^+ + 2e^-$</td>
<td>$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$</td>
<td>$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$</td>
</tr>
<tr>
<td>DMFC</td>
<td>$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$</td>
<td>$1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$</td>
<td>$2CH_3OH + 3O_2 \rightarrow 4H_2O + 2CO_2$</td>
</tr>
<tr>
<td>MCFC</td>
<td>$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$</td>
<td>$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$</td>
<td>$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$</td>
</tr>
<tr>
<td>SOFC</td>
<td>$H_2 + O_2^2- \rightarrow H_2O + 2e^-$</td>
<td>$\frac{1}{2} O_2 + 2e^- \rightarrow O_2^2-$</td>
<td>$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$</td>
</tr>
</tbody>
</table>
Table 1.3 Impact of fuel constituents on the performance of various fuel cells [7,8]

<table>
<thead>
<tr>
<th>Gas Species(^a)</th>
<th>PEMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>DMFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2)</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
<td>NA</td>
<td>Fuel</td>
<td>Fuel</td>
</tr>
<tr>
<td>(\text{CO})</td>
<td>Catalyst Poison ((&gt; 10 \text{ ppm})^b)</td>
<td>Poison</td>
<td>Catalyst Poison ((&gt; 0.5%))</td>
<td>Catalyst Poison</td>
<td>Fuel (^c)</td>
<td>Fuel (^c)</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
<td>Diluent</td>
<td>Poison</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent (^d)</td>
<td>Fuel (^d)</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>Diluent (^e)</td>
<td>Poison</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent ((\text{essential at cathode}))</td>
<td>Diluent</td>
</tr>
<tr>
<td>(\text{S as (H}_2\text{S &amp; COS)})</td>
<td>Catalyst Poison</td>
<td>Poison</td>
<td>Poison ((&gt; 20 \text{ ppm for H}_2\text{S}) (&gt; 50 \text{ ppm for COS}))</td>
<td>Poison</td>
<td>Poison ((&gt;0.1-5\text{ppm}[4]))</td>
<td>Poison ((&gt;0.1 \text{ ppm}))</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>Membrane Poison</td>
<td>Electrolyte Poison ((&gt;0.2%))</td>
<td>Relatively harmless ((&lt;1.0%))</td>
<td>Relatively harmless ((&lt;0.5%))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{HCl, other halides})</td>
<td>Poison</td>
<td>Poison ([4,5] 0.1-1 \text{ ppm})</td>
<td>Poison ((&lt;0.1 \text{ ppm}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si})</td>
<td>Catalyst Poison</td>
<td>Catalyst Poison</td>
<td>Probably Anode</td>
<td>Anode Poison</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.5 Materials used for Solid Oxide Fuel Cells

The importance of materials selection in SOFCs comes from the fact that their operating temperature is very high. Besides being good conductors of electrons and ions, there are some other properties, which the materials should possess to ensure the long term and stable operation of the cell. Apart from high strength of the materials, the thermal expansion of the electrodes, electrolytes and interconnects should be similar. The interconnect and electrolyte must be dense enough to prevent gas mixing and the electrodes should be porous enough to allow the gas transport. Other significant properties are related to the ease of manufacture and low cost.

**Electrolyte:** Zirconia doped with 8-10 mole % of yttria (yttria-stablisled zirconia) is mainly used as electrolyte because of its high conductivity of oxygen ions and stability in both oxidizing and reducing environments. The property of conduction of oxygen ions is due to the fluorite structure of zirconia in which some Zr$^{4+}$ ions are replaced by Y$^{3+}$ ions leaving some O$^{2-}$ sites vacant. These vacancies make O$^{2-}$ ions from the cathode travel across the electrolyte of the cell. The ionic conductivity of yttria-stablisled zirconia compares to the liquid electrolyte and it can be made as thin as 25-50 $\mu$ m to reduce ohmic losses. A small amount of alumina is also added to provide to increase the mechanical stability to the electrolyte.

**Anode:** The anode of a SOFC is a cermet (mix of a metal and heat resistant compound) made by adding metallic nickel in the yttria-
stabilised zirconia skeleton. The yttria-stabilised zirconia provides stability and high porosity (20-40%) for the anode gases and the metallic nickel provides conductivity to the electrons and. The thermal expansion coefficient of anode material is close to that of the electrolyte.

**Cathode:** Similar to the anode, the cathode of a solid oxide fuel cell should possess ionic and electronic conduction, stability at high temperatures, high porosity, and appropriate thermal expansion coefficient. Strontium doped lanthanum magnetite (La$_{0.84}$Sr$_{0.16}$MnO$_3$) a p-type semiconductor is most commonly used material for the cathode.

**Interconnect:** The interconnect in a SOFC is used to connect individual cell units in series. In a planar SOFC stack, it is also known as bipolar plate as one side of it is in contact with the cathode and the other side with the anode. Apart from conducting electrons from the anode to the cathode, it provides space for the flow channels for air and fuel. The arrangement is different in a tubular SOFC. Choosing the right material for the interconnect is a difficult task due to its high operating temperature of the SOFC (800 to 1000°C): conventional metals like steel differ in thermal expansion coefficient with the yttria-stabilised zirconia electrolyte. One material that suits, “inconel” type stainless steel, tends to be very expensive. Other metals tend to form an oxide coating, which limits their electrical conductivity and act as a barrier to the mass transport in the flow channels [8]. Lanthanum
chromite, which is basically a ceramic, is commonly used for tubular designs of SOFCs. The conductivity of the material is increased by doping it with magnesium or other alkaline earth elements. Most of the fabrication methods of these alloys are proprietary and rigorous research is going on in this field.

1.5.1 Practical Designs and Stacking

The three main SOFC arrangements are: tubular, planar and monolithic. These arrangements differ in their complexity, losses, power density and sealing methods. The highest power density is achieved with the monolithic design of SOFC, which looks like a corrugated card box in its cross section. However, difficulties with thermally induced tensions and with the sealing, which cause the breaking of the cell, favor the tubular, planar or the combination of the two arrangements.

**Tubular Design:** Siemens Westinghouse Power Corporation first developed the tubular design of a solid oxide fuel cell. Figure 1.1 shows the schematic and stacking arrangement of the cell. The cell unit is in the form of a hollow cylindrical tube closed at one end. Cathode, electrolyte, anode, Air channel and fuel channel are arranged in layers from the center to the periphery. In this design of the fuel cell, thin layers of electrolyte and anode are deposited on a cathode tube. The tube is produced by extrusion and sintering. A strip of interconnect is tightly attached to the cathode of the cell and the
other end of it is in contact with the anode of the adjacent cell unit. Air is supplied in the inner tube flow channel and fuel to the free side of the anode.

Figure 1.1 Tubular SOFC Developed by Siemens Westinghouse (left) and the Stacking of the Cells (right). (Siemens Westinghouse)

Figure 1.1 (right) shows a tubular fuel cell stack developed by Siemens Westinghouse, which consists of 24 tubes (each 2.2cm diameter and 150cm in length) connected in series[8].

**Planar Design:** Planar solid oxide fuel cells are currently produced by many companies. Several geometries have been developed such as circular, quadratic or rectangular. Each unit consists of flat plates of interconnect, cathode, electrode and anode and these units are put side by side to form cell stack as shown in the Figure 1.2

Many flow arrangements exist in a planar SOFC, such as cross-flow, parallel flow and counter flow. The co-flow arrangement is the most favorable design in terms of thermal stresses where as the counter flow is the least favorable in terms of thermal gradient but it
is most commonly used designing due to the less complicated manifolding and the reduced constraints of sealants.

![Figure 1.2 Flat Plate SOFC Unit (Craig Fisher)](image)

Advantages of planar SOFC design are ease of manufacture, simple design and high power density [8].

**Integrated planar SOFC and tubular SOFC design:** Integrated planar SOFC design by Rolls Royce Company utilizes the features of both planar and tubular SOFC. It consists of an assembly of planar SOFCs fabricated in a ceramic housing which provides manifolding for the fuel gas and there are no separate bipolar plates instead interconnects are fabricated on to the cell housing itself [8].

As mentioned earlier that maximum work that can be produced from a fuel cell is equal to the Gibbs free energy change of the chemical reaction occurring in the cell. Figure 1.3 shows how fuel cell and heat engines efficiencies vary with temperature and how the combined cycle always gives a better efficiency.

From the **Figure 1.3**, we can understand the potential of hybrid power systems. Traditional heat engines need to operate at really high
temperatures to achieve high thermal efficiencies and the losses are higher in fuel cells at low temperatures. But at high operating temperatures, fuel cells combined with heat engines approach the maximum theoretical efficiency.

![Figure 1.3 Comparison of Heat Engine, Hydrogen Fuel Cell and Combined Hybrid System Efficiency [8]](image)

**Figure 1.3 Comparison of Heat Engine, Hydrogen Fuel Cell and Combined Hybrid System Efficiency [8]**

### 1.6 Gas Turbine

A gas turbine cycle works on Brayton cycle, which is a simple series of compression, combustion, and expansion processes. The main components of the Brayton cycle are a compressor, a combustor, and a gas turbine. The number of components is not limited to three as
the cycle may consist of several compressors and turbines. Figure 1.4 shows the basic schematic diagram of a gas turbine cycle. The ambient air is compressed in the compressor and supply to the combustor. The constant pressure combustion takes place and the high temperature gas is sent to the gas turbine where power is produced to drive the compressor and the generator. Heat exchangers can be used to preheat the stream entering the combustor.

![Diagram of a Gas Turbine Engine Based Upon the Brayton Cycle](image)

**Figure 1.4 Schematic of a Gas Turbine Engine Based Upon the Brayton Cycle**

Gas turbine engines are generally used for power production falling in the range of fewkWs to several MWs and offer an electrical efficiency of 35-40%. This can be further improved by adding a topping cycle to achieve up to 60% efficiency.

A gas turbine can be directly or indirectly connected to the Solid
Oxide Fuel Cell. In an indirect integration, the combustor of the gas turbine is replaced with a heat exchanger in which air from the compressor is heated by the fuel cell exhaust and the Solid Oxide Fuel Cell can operate under atmospheric conditions. Although, it reduces the sealant requirement in the Solid Oxide Fuel Cell stack, the heat exchanger has to operate at very high temperatures and pressure differences. The material requirements in the indirect integration are really an important issue and hence, it is not generally used.

Figure 1.5 shows a direct integration of a solid oxide fuel cell and a gas turbine system. As can be seen from it, the combustion chamber of the gas turbine engine has been replaced with a Solid Oxide Fuel Cell and an afterburner. The pressurized air from the compressor goes

**Figure 1.5 Gas Turbine Engine as a Bottoming Cycle in a GT-SOFC System [8]**
into the Solid Oxide Fuel Cell. The exhaust from the Solid Oxide Fuel Cell goes to the afterburner and the resulting high temperature and pressure exhaust gas enters into the turbine. In this case, the Solid Oxide Fuel Cell operates at high pressure, which further improves its performance. Moreover, heat exchangers are added after the turbine exhaust to further recover the waste heat in preheating of the streams entering the Solid Oxide Fuel Cell stack. The high-pressure operation of Solid Oxide Fuel Cell stack causes large pressure gradients between anode and cathode. This pressure imbalance needs to be avoided, due the brittleness property of the Solid Oxide Fuel Cell materials, and good sealants are required to stop leakages [9, 10].

1.7 Other Plant Components

Depending upon the fuel used and the chosen configuration, stable operation of Solid Oxide Fuel Cell - Gas Turbine systems may require components that have not been discussed so far.

1.7.1 Fuel Processing

One important feature of high temperature fuel cells is that they can work with many other fuels like natural gas or any other hydrocarbons. Solid oxide fuel cells, operating on heating oil, fermentation, methanol, formic acid [11], gasified coal and biomass, have also been presented. All of these fuels produce hydrogen through chemical reactions that occur at temperatures usually above 500°C
and are endothermic. The heat required by the reforming reactions is provided by the fuel cell.

**Desulphurisation:** It is necessary for some fuels like natural gas and other petroleum gases to go through the desulphurization process before any further fuel processing is done. These fuels generally contain sulphur in the form of organic compounds or $H_2S$, which acts as a deactivator for the steam reforming catalysts and shift reaction catalysts [8]. Any organic sulphur-containing fuel is converted to $H_2S$ in the presence of nickel-molybdenum oxide catalyst or cobalt-molybdenum oxide catalyst via “hydrogenolysis reactions” of the type:

$$ (C_2H_5)_2S + 2H_2 \rightarrow 2C_2H_6 + H_2S $$ \hspace{1cm} (25)

the $H_2S$ that is formed by such reactions is converted to zinc sulphide over a zinc oxide bed:

$$ H_2S + ZnO \rightarrow ZnS + H_2O $$ \hspace{1cm} (26)

**Steam reforming:** Any fuel that is used in Solid Oxide Fuel Cell has to be converted to hydrogen and carbon monoxide and the method that is generally practiced is the steam reforming. The basic reforming reactions from methane and other hydrocarbons $C_mH_n$ are:

$$ CH_4 + H_2O \rightarrow CO + 3H_2 \quad [\Delta H = 206kJ / mole] \hspace{1cm} (27) $$

$$ C_nH_m + nH_2O \rightarrow nCO + (m / 2 + n)H_2 \hspace{1cm} (28) $$

$$ CO + H_2O \rightarrow CO_2 + H_2 \quad [\Delta H = -41kJ / mole] \hspace{1cm} (29) $$

The reforming reactions 27 and 28 are called as *oxygendysis reactions* and reaction 29 as *water gas shift reaction* and generally occur in
presence of nickel catalyst in a SOFC at temperature above 500°C. These reactions are reversible and reach equilibrium state very fast over the active catalyst. The combination of chemical reactions 27 and 28 makes sure that the overall product is a mixture of mainly CO, H₂, and CO₂ together with remaining methane and steam [8].

There are two methods of steam reforming: “direct internal reforming” and “indirect internal reforming”. When the reforming reactions take place directly over the anode of the Solid Oxide Fuel Cell, reforming is termed as Direct internal reforming. Direct internal reforming often better utilizes the steam and provides a higher degree of thermal integration but it increases the system complexity. In the case of indirect internal reforming, there is a separate reformer, which is either thermally integrated with the stack or to an external heat supply [8].

1.7.2 Combustor

The combustor in a Solid Oxide Fuel Cell – Gas Turbine hybrid power system is used after the fuel cell stack to burn the remaining fuel. The combustor should be specifically designed for the hybrid system; a commercial combustor cannot be used because the exhaust from the Solid Oxide Fuel Cell has a very low calorific value and diluting air is not at once available at sufficient temperature. However, combustors specifically designed for Solid Oxide Fuel Cell can operate over a large range and at the same time achieve very low emissions [12].
1.7.3 Heat Exchangers

Heat exchangers in a Solid Oxide Fuel Cell system are of great importance since the gasses entering the Solid Oxide Fuel Cell need to be preheated for better performance and to reduce thermal stress in the stack. The heat exchangers also affect the overall efficiency and optimum operating pressure of the system.

1.8 Fuel Cell based combined Cycle Power Plants:

Fuel cells use hydrogen, or hydrocarbon fuels, together with oxygen form atmospheric air, to produce combined heat and power (CHP). There are different types of fuel cell based power generation systems, depending on type of fuel cell and fuels used. Polymer electrolyte membrane FC (PEMFC) can be used for powering automotive vehicles or for stationery power generation. PEMFC need pure H\textsubscript{2} fuel and produce no CO\textsubscript{2} emissions in the reaction. It is sensitive to poisoning. They operate at low temperature (80-150ºc) and offer an efficiency of 35% - 40%. Molten Carbonate Fuel Cell (MCFC), Solid Oxide Fuel Cell (SOFC) and Phosphoric Acid Fuel Cell (PAFC) are used for combined heat and power generation. SOFC and MCFC are usually fuelled by either hydro carbons or H\textsubscript{2}. MCFC and SOFC operate at high – temperatures 650 ºc and 800 - 1000 ºc respectively. SOFC offer the highest electrical efficiency (44%-50%) and exceeds 80% in combined cycle mode. Direct Methanol Fuel Cell (DMFCs) are the best option to replace batteries in Portable electronic devices, since methanol is
easily transportable. Their efficiencies are between 15% and 30%. Fuel Cell research is focusing on life time and performance of the Fuel Cells.

A combined cycle power system consists of a combination of two or more power generation technologies to make best use of their optimum operating characteristics and to obtain efficiencies higher than that could be obtained from a single power cycle. Fuel Cells directly convert the fuel and an oxidant (from air) into electricity through an electrochemical reaction and produce very low emissions and have higher operating efficiencies. Therefore, integrating fuel cells with other power sources, the efficiency of the combined system can be further increased. The different types of fuel cell based combined cycle power plants are:

1. High temperature SOFC – Gas turbine combined cycle power plant
2. High temperature SOFC – Thermophotovoltaic (TPV) combined power plant.
3. High temperature GT – MCFC combined cycle power plant
4. High temperature MCFC – Thermophotovoltaic (TPV) combined cycle power plant.
5. PEM fuel cell – solar power combined cycle power plant.
6. PEM fuel cell – wind power combined cycle power plant.
7. Hybrid fuel – cell system with wind and solar power.

In the above systems, in the first four plants, high temperature Fuel Cells are combined with another power generation system to
increase the combined efficiency of the system. In the remaining three systems, FCs and another power generating system are combined to best make use of the operating characteristics of the individual systems to either supplement the fuel cell power or to extend the duration the availability of power.

1.9 Other types of Combined Cycle Power Plant:

When two power cycles are connected in series, in such a way that the heat rejected form cycle topping one, is supplied to the second cycle (bottom), then the overall thermal efficiency of the combination would be higher than the individual single cycle efficiency. A series of such plants were developed by the General Electric of the USA [14] in the 1940s culminating in the installation of the Schiller 40 MW plant at Portsmouth, New Hampshire which generated power in 1950. The Thermal efficiencies of these plants are high (>50%). 1970s, a number of companies have developed combined cycle power systems in package form. Westinghouse designed a unit, called PACE an acronym for power at combined efficiencies). The GE system is called STAG (an acronym for steam and gas turbines) and the Firm of Stone and Webster has developed a combined-cycle system called FAST. [15]

The combined-cycle power systems appear to be very promising for the so-called intermediate load service between the peak load units (gas turbines and Diesel engines) and the base load units (large fossil-
fuel or nuclear steam power plants). These plants also offer the advantage of producing power very quickly (<20 min).

There is a great thermal irreversibility and a decrease of availability because of heat transfer from flue gasses (1300°C) to steam (600°C) through a large temperature difference. By integrating a high temperature power plant as a topping unit to the steam plant, a higher energy conversion efficiency from fuel to electricity can be achieved, since the combined plant operates through a higher temperature range.

Combined cycle power plants may be of the following types:

1.9.1 **Gas Turbine-steam turbine plant**:

It consists of two cycles called Brayton Cycle and Rankine cycle. Rankine cycle is used as bottoming cycle in which the steam in the working fluid and Brayton cycle is used as topping cycle in which gas is the working fluid. This plant can be filled with either gaseous fuels like natural gas, methane, coal gas etc. or liquid fuels like Diesel, Petrol, Kerosene etc. Solid fuel like coal can also be used as fuel. In this, gas turbine plant can be either open or closed. There are many coal based combined cycle power plants which are operating in India and the World.

1.9.2 **Coal-based combined cycle plants**:

Coal is a low grade fuel when compared to natural gas and oil, but coal reserves are very large and much effort has been made to develop clean coal technologies.
There are two types of coal-based technologies

1. Pressurized Fluidized (either a bubbling or a circulating) bed combustion (PFBC) system,

2. Integrated Gasification Combined Cycle (IGCC)

1. PFBC – Combined Cycle : - In this system, a pressurized fluidized bed combustor (PFBC) is used to supply hot gas at high pressure to a gas turbine through a hot gas clean-up system. Line stone and coal are supplied to the pressuring combustor. The limestone is used as the bed material which absorbs sulphur. Cooling tubes are immersed in the fluidized bed which are used to generate high pressure steam supplied to steam turbine. The combustion products leaving the combustion chamber are passed through a clean-up system before being expanded in the gas turbine. The exhaust gases, than passed through an economizer which heats the feed water before being discharge. The temperature in the PFBC is limited to about 850ºc because this is the most feasible temperature of sulphur retention and it is below the ash fusion temperature of most coals.

2. IGCC : - Coal is gasified either wholly or partially and the syngas produced after clean-up is burnt in the combustion chamber of the gas turbine. The limestone and coal are fed to the pressure vessel, the coal is being gasified by steam and oxygen. A gas of lower calorific value is produced by the use of oxygen instead of air. The exhaust gases from the gas turbine produce steam in the Heat
Recovery Steam Generator (HRSG). The thermodynamic performance of an IGCC power plant studied by Wag and De [16] which shows that there is an optimum Pressure Ratio for the gas cycle at a given temperature ration of the maximum overall combined cycle efficiency. The British Coal “Topping Cycle” in the combined Cycle Power plant allows the gas turbine inlets temperature to the increased considerably higher than 850ºc by burning fuel gas produced by partial gasification of the coal. Char from the gasifier is burnt in the PFBC to raise the temperature of hot gas and generate steam. A gas turbine inlet temperature of about 1200ºC results in a significant increase in the efficiency of the combined cycle.

A.I. Kalina proposed a combined cycle with Novel Bottoming Cycle in which a mixture of water and ammonia is used as the working fluid. An energy analysis of the Kalina Cycle was made by Nag and Gupta [17] to find the optimum ammonia concentration at the steam turbine inlet.

1.9.3 Combined Magneto-hydrodynamic (MHD) generator:
In this plant MHD generator replaces the gas turbine unit as the power producing unit in the topping cycle. In an MHD generator, the hot ionized gas or plasma replaces the copper windings of an alternator. When a gas is heated up to high temperatures, the valence electrons of the exited atoms move on the higher energy orbits and
finally, at certain energy levels they move off and become free electrons. For a conducting gas, a certain no. of free electrons must be present along with the body of natural atoms and an equal number of ions. An electric field is created in a direction normal to both the magnetic field and the duct axis, when the strong magnetic field passes across the flow passage in a direction perpendicular to the direction of flow. Unfortunately MHD generator power output is restricted because the electrical conductivity of gas becomes very low when the temperature of gas falls to 2000ºc. Therefore this is used as topping cycle and the exhaust form MHD at about 2000ºc is utilized in generating steam to derive the steam turbine and generate electricity in a conventional steam power plant used as a bottoming cycle.

1.9.4 Thermionic – Steam Power Plant : -
A thermionic generator converts heat directly into electricity by utilizing thermionic emission. Metal have free electrons. A metal electrode, called as an emitter, is heated up until it is hot enough to release electrons from its surface. The electrons flow through a small gap and accumulate on a cooled metal electrode, called as collector. In order to minimize the energy losses as electrons pass through the gap, the space between the two electrodes is either maintained at a high vacuum or filled with a highly conducting fluid like ionized cesium
vapour. The electrons enter the cooler anode and return to the hot cathode through an external load, thus producing electric power.

In the boiler of the steam power plant, the riser tubes are located in the radiation zone of the furnace. The heat energy of high temperature combustion gases can be partly converted to electricity if the riser tubes are provided with anode and cathode of a thermo-ionic generator with the gap filled with ionized cesium vapour. Thus the overall plant efficiency will be increased. Another useful application is in a topping cycle, combining an MHD generator with a thermionic generator. The temperature of waste heat from an MHD generator is often as high as 1900 °C. The thermionic generator could utilize this heat prior to its use in a conventional steam power cycle. Then it becomes a combined MHD – thermionic – Steam power plant.

1.9.5. Thermoelectric – Steam Power Plant: -
Thermo couple works on the principle of seebeck effect which states that when the junctions of two dissimilar wires are maintained at two different temperatures a potential difference is developed. This is the basis for temperature measurement. A thermoelectric generator is similar to the thermocouple, but the thermo elements are made up of semiconducting materials P and n and the heat is supplied to the hot junction and removed at the cold junction, both the junctions are made up of copper. The waste heat of diesel engines and gas turbine can be utilized for thermoelectric power generator. Also the stack
gases can be used to produce electricity by thermoelectric means. The metal stack consists of a series of rings of two alternate metals connected alternately at the outer and inner annular edges and are electrically and thermally insulated. The cumulative voltage can be produced by the pairs of a series of thermo electrodes. A thermoelectric generator can be integrated in the nuclear reactor fuel elements to obtain large power output. It can be used as topping cycle to a conventional steam plant. The overall efficiency of the combined cycle would be increased with the higher operating temperature range.

1.10 Thesis Outline:

The thesis consists of seven chapters. The first chapter includes the status of power generation in India and World and the combined cycle power plants based gas turbines / steam turbines and fuel cells. This chapter also describes the comparison among the different types of fuel cells. Chapter 2 provides the Literature review on GT-SOFC systems and GT-MCFC hybrid power systems. Chapter 2 also includes the objectives of the present work. Chapter 3 deals with the modeling of GT-SOFC combined cycle power plant for different fuels like Methane, Natural Gas, Coal Gas and Ethanol with the model calculations of temperatures, pressures, exergy of the working fluid, the irreversibility of the each component of the system, thermal efficiency and the exergy efficiency of the system. Chapter 4 describes the modeling of GT-MCFC combined cycle power plant for different
fuels. It also includes the working principle of the MCFC. In Chapter 5, the results of a parametric study of the GT-SOFC combined cycle and the GT-MCFC combined cycle power plant for different fuels. Chapter 6 includes the conclusions derived from the present research work. Chapter 7 gives the recommendations for future work.