# 1

# Introduction

## 1.1 Energy and Membranes

Energy crisis, water and food shortage, environmental pollution, and so on are important problems of human beings for the next 50 years. Energy crisis is the single most important problem because of an increase in energy usage from the technological development and its influence on energy toward water, food shortage, and environmental pollution. According to International Energy Outlook 2021 (International Energy Association 2021) from the United States Energy Information Administration (EIA), the world energy consumption will grow by nearly 50% between 2020 and 2050. Most of this growth comes from regions where strong economic growth is driving demand, particularly in Asia. Demand for all fuels increased, with fossil fuels meeting nearly 70% of the growth for the second year running. As a result, global energy-related $CO_2$ emissions rose by 1.7% to 33 gigatons (Gt) in 2018. Coal use in power generation alone surpassed 10 Gt, accounting for a third of total global $CO_2$ emission. Most of that came from newly built coal-fired power plants in developing countries [1]. As the amount of energy consumption increased enormously, in particular, after the Second World War, there was a worldwide issue on energy consumption and production that raised intensive environmental issues (see Figure 1.1). The largest portion of the energy sources are fossil fuels such as coal, oil, and natural gas that cover more than 80% of all the energy sources.

To solve the energy crisis, various efforts have been made to economically produce energy and use it efficiently. From fossil fuels to renewable energy, various kinds of resources have been utilized to produce energy. Fossil fuels are hydrocarbons, primarily coal, petroleum, or natural gas, generated from buried combustible geologic deposits of organic materials that have been converted to petroleum, coal, and natural gas by heat and pressure in the earth's crust over hundreds of millions of years. Because of their origin, fossil fuels have a high carbon content, resulting in a high heat content. According to the Statistical Review of World Energy from British Petroleum in 2020, the main primary energy sources worldwide consisted of coal (24%), petroleum (33%), and natural gas (27%), amounting to an 84% share for fossil fuels in primary energy consumption in the world [2]. Fossil fuel is the most economic resource to produce energy; however, it is required to reduce the share

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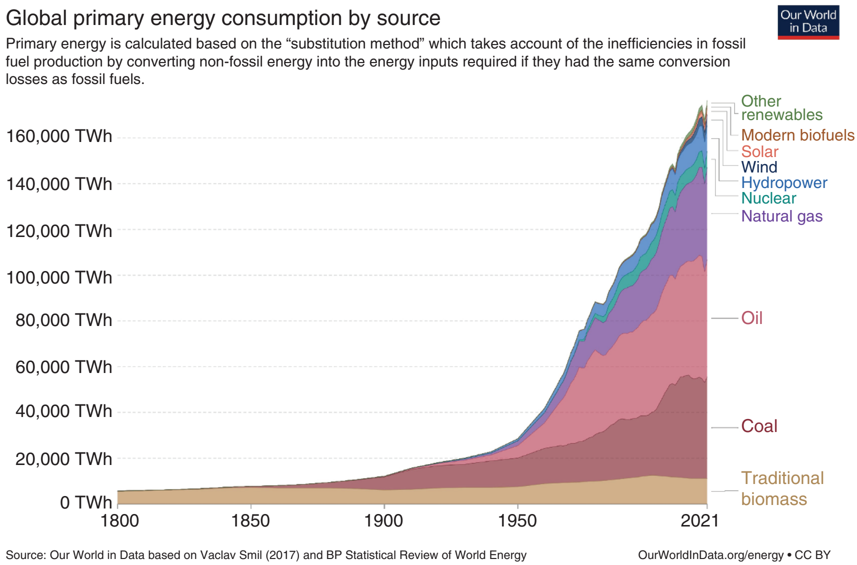


**Figure 1.1** Global primary energy consumption by source.

of fossil fuel due to emission of $CO_2$ inducing global climate change. Currently, technology innovation is applied as a means to decrease the environmental impact of coal combustion by increasing the boiler efficiency, co-combustion with biomass or carbon capture, utilization, and storage [3]. Nuclear power is one of the candidates to replace fossil fuels owing to its low price for energy production. However, it is hard to completely replace fossil fuels with nuclear power due to its drawbacks such as uncertain accidents and the production of radioactive nuclear wastes. Especially, the three nuclear disasters (that is, Three Mile Island in 1979, Chernobyl in 1986, and Fukushima in 2011) caused by human mistakes and/or natural disasters such as flood and earthquake make it difficult to expand the number of nuclear power plants. Renewable energy including solar, wind, and geothermal energy has been developed during the last decades with an infinite potential; however, they require further research to overcome their limitations such as low energy density, intermittent energy production, and so on. As such, each energy resource has strengths and possibilities; however, it also has weaknesses to be solved.

Let us briefly look at the conversion of fossil fuels to electrical energy. Thermal power plants use coal, petroleum, and natural gas as fuel. According to the species and phases of the fuel, transportation of the fuel to the plant and post- and pre-treatment of the fuel are different resulting in the application usage. However, the principle of generating electricity from fossil fuels is the same. The steam is produced at a high pressure in the steam boiler after burning fuel in boiler furnaces. Superheated steam then enters into the turbine and rotates the turbine blades. The turbine is mechanically coupled with alternator that its rotor will rotate with the rotation of turbine blades. After entering into turbine, the steam pressure suddenly falls and the corresponding volume of the steam increases. After imparting energy to the turbine rotor, the steam passes out of the turbine blades into the condenser. In the condenser, cold water is circulated with the help of a pump which condenses the low-pressure wet steam. This condensed water is further supplied to a low-pressure water heater where the low-pressure steam increases the temperature of this feed water and it is again heated at high pressure. The chemical energy in fossil fuels is converted to thermal energy through carbon and hydroxide combining with oxygen during the combustion. Heat energy boils pressurized water to steam, and the steam travels through a mechanical turbine, causing it to rotate converting thermal energy to electric energy, i.e. electricity.

Pulverized coal (less than 5 cm) is burned in a boiler where water boils to steam. Converted steam is used to operate turbines for electronic generators. Compared to thermal power plants using other fuel types, coal requires a specific fuel processing and ash disposal. Flue gas from the combustion of fossil fuels contains carbon dioxide ($CO_2$) and water vapor, as well as pollutants such as nitrogen oxides (NOx), sulfur oxides (SOx), and, for coal-fired power plants, mercury, traces of other metals, and fly ash. Solid waste ash from coal-fired boilers should be removed. Gas-fired power plants, which burn natural gas (mainly methane) to generate electricity, produce a quarter of the world's electricity; however, they are also a significant part of global greenhouse gas emission resulting in global warming.

As the majority of current global primary energy relies on fossil fuels, the energy system is the source of approximately two-thirds of global $CO_2$ emissions. As methane and other short-lived climate pollutant emissions are believed to be severely underestimated, it is likely that energy production and use are the source of an even greater share of emissions.

Meanwhile, membrane technology, which has been able to be utilized with various kinds of energy application, has been developed to solve the water issues and the problems of energy production. For example, in energy production using fossil fuels, membrane technology can be utilized to reduce the environmental impact from the emission of carbon dioxide. Membranes can separate the carbon dioxide from the ash inducing environmental issues and prevent them from being discharged to the outside. Moreover, membrane technology is also used as an integral part of the energy production in various ways. For example, in a fuel cell application, membrane performance determines the overall system performance including power density and long-term stability of the fuel cells. In energy production using salinity gradients and osmotic pressure, membranes enable the harvesting of blue energy from the ocean, induced by the chemical potential difference using the diffusion difference of water and salt.

## 1.2 Brief History of Membrane Technology

Membrane technology has been known for a long time. The first report on gas separation was made by Mitchell [4], who observed the separation of gases through membranes. He noticed that gases had different permeabilities in experiments using rubber balloons exposed to various gas atmospheres. Graham [5, 6] reported in 1829 about different rates of permeation in experiments where a wet pig bladder inflated when stored in $CO_2$ environment. Fick established the theoretical equations for diffusion through membranes. Graham proposed the concept of solution–diffusion as the permeability process in polymeric membranes in 1866 [7]. Daynes [8] established a time lag method to determine diffusion coefficients employing the unsteady-state solution of Fick's second law to mathematically determine the diffusion coefficient from the extrapolation of the steady-state flux to the time axis. Barrer and Rideal [9] noted the temperature-dependent Arrhenius equation of gas permeability and diffusion of gases. Although most of these scientific advances have enlightened the membrane community, historic advances in gas and liquid separation membranes occurred in 1960 with the discovery of asymmetric cellulose acetate membranes with a selective layer thickness <1 μm for reverse osmosis by Loeb and Sourirajan [10–12]. Before this discovery, dense cellulose acetate membranes separated water and salts but were too thick to produce sufficient water flux to meet the commercial needs [13]. The production of asymmetric cellulose acetate membranes spurred the commercialization of reverse osmosis membrane and later led to gas separation membrane [14, 15]. A thin polyamide layer of 0.2 μm thickness can be coated on top of a microporous polysulfone support layer with a thickness of 200 μm to produce a thin-film composite membrane for reverse osmosis and nanofiltration [16]. The same concept of thin-film composite membrane can be applied to produce integrally skinned asymmetric membrane by depositing or coating selective dense layer on top of a porous sublayer [17].

The first commercial gas separation membrane system was introduced by Hennis and Tripodi [18, 19] at Monsanto to produce hydrogen in an ammonia synthesis plant. Membrane-based gas separation is being considered for carbon capture and storage of flue gas evolved from coal-fired power plants to meet the requirements of global climate change [20, 21].

The market for polymer membranes for gas and liquid separation has been expanding annually. The sales of membrane gas separation systems were approximately US$ 846 in 2019 and projected to be US$ 1132 million in 2024 at a CAGR of 6%. The worldwide sales of all synthetic membranes are estimated to be over US$ 5.4 billion as of 2019 and projected to grow to US$ 8.5 billion by 2024, at a CAGR of 9.0%. These numbers exclude the membranes for energy generation applications such as lithium-ion batteries and fuel cells. The main reasons for the fast growth of membrane markets and sales include consumer demand for higher quality products, increased regulatory pressures, deteriorating natural resources, and the need for environmental and economic sustainability. The major drivers for the membrane market include increasing population, raising awareness about wastewater reuse, and rapid industrialization. Also, the shift from chemical treatment of water to physical treatment of water, strict regulations regarding water treatment and discharge, and changing climate dynamics in terms of the amount of precipitation are also driving the membrane market. The future market is expected to expand, and further growth of this technology is anticipated for the next 10 years or so.

It is interesting to note that energy can be produced using membranes, for example, by using hydrogen as a fuel. Fuel cell concept was first demonstrated by

William Grove in 1839 using an experiment applying hydrogen and oxygen [22]. Water is electrolyzed into hydrogen and oxygen by passing an electric current through it. A fuel cell acts as an engine as it is a device that converts chemical energy into useful work, whereas a combustion engine converts the chemical energy of the fuel and oxidizer into mechanical work. The first fuel cell was developed by General Electric in the United States for the US Gemini space program in the early 1960s [23]. The fuel cell was expected to provide electricity and water for an animal orbiting in space in a satellite. The development of the space program continued with the incorporation of a new polymer, Nafion. DuPont and General Electric looked into the application of Nafion that received much attention due to its use as an electrolyte in the proton exchange membrane fuel cell (PEMFC) [24].

The same Nafion membrane was used in proton exchange membrane water electrolysis (PEMWE). The first PEMWE using this polymer began to be commercialized in 1978 [25]. Because of the use of expensive catalyst and membrane, an alternative to PEMWE was proposed, i.e. anion exchange membrane water electrolysis (AEMWE). Although many membrane materials have been tested, large-scale commercial AEMWE needs more time to appear.

We are living in an age of electrical vehicles. About 10% of the new cars are electrical vehicles equipped with lithium-ion batteries. European countries will ban the cars equipped with internal combustion engines by 2030, and this trend is moving forward to other countries. The proportion of electrical vehicles in total automobile market will exceed 30% by 2030, where LIB demand accounts to be 1293 GWh [26]. Batteries are made of many components such as cathode, anode, electrolyte, and separator. Separator is a porous membrane made mainly of polyolefins. Separator production in 2025 is estimated to be 2.7 billion $m^2$ with a CAGR of 12% [27]. Separators are made by dry process and wet process.

### 1.2.1 Current State-of-the-Art Membrane Technology

Membrane-based gas separation is currently being used to separate hydrogen from ammonia plants, oxygen from air, nitrogen from air, $CO_2$ from nitrogen stream or methane mixture, volatile organic compounds from petrochemical plants, water from organic vapors, and isopropanol from semi-conductor plants. For these applications, membranes are in hollow fiber or flat sheet forms that are constructed to make modules. Polysulfone, polyimide, and cellulose acetate are the most widely used membrane materials in industry while many microporous materials are under investigation mainly in academia.

PEMFC is currently utilized in fuel cell automobiles or vehicles while direct methanol fuel cell is used in forklifts. These membranes use perfluorosulfonic acid (PFSA) membranes. Solid oxide fuel cell or metal ceramic fuel cell is used in electricity generation for households or small residential areas.

PEMWE is currently being used in generating hydrogen. This technology also uses PFSA as a membrane. Proton exchange membranes are incorporated to fabricate membrane electrode assembly where catalysts are coated on each side of the membrane. To reduce the cost of membrane and catalyst in PEMWE, AEMWE is evolved these days. A lot of progress has been made in AEMWE which will soon be commercially available.

Separator is an exploring market and has been widely used in LIB manufacturing. Polyethylene or polypropylene has been used to manufacture LIB separators. Ceramic coating technology is widely used to increase the thermal stability of the separator. Other high-performance polymers are considered for separator materials, but the cost of the separator hinders the widespread of these materials for separator. Dry extension and wet manufacturing technology are the two major technologies widely used in the separator manufacturing industry.

Fuel cells and battery separators use membranes in flat sheet type which can be fabricated in stack or module form.

Throughout this book, we will introduce various kinds of membrane technologies for energy application, from their history to the recent development. We will also describe how membrane separations compare with other separation methods, and bring the readers to the current state of the art.

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