

ACADEMIC APPROACHES TO ENGINEERING ISSUES

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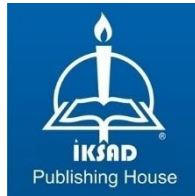
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PREFACE

In this book, especially today's engineering issues are evaluated from an academic perspective. In this respect, it shows in the theoretical and experimental analysis of engineering problems for both engineers and academics. It is aimed to reach a wide range of researchers with the eight different sections included. We hope that the book, which touches on global problems such as solid waste problems, renewable energy sources, and energy storage systems associated with today's engineering issues as well as the electron microscope and masonry buildings, which have gained much attention in recent decades, will be useful to researchers and academics working on these research areas.

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CHAPTER 1

**PREPARATION OF REFUSE DERIVED FUEL (RDF) AND
ITS' STAGES**

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1. INTRODUCTION

Nowadays, municipal solid waste (MSW) is disposed of most appropriately with waste management thanks to advanced technologies, which brings with a large energy conversion. As known, disposal technologies include various systems such as pyrolysis, gasification and combustion and etc. On going studies of systems and goals to achieve better innovations in the field of fuels. They developed different types of fuels with different characteristics which obtained from municipal solid wastes- Which is called refuse-derived fuel (RDF).

2. REFUSE-DERIVED FUEL (RDF) DEFINITION

The disposal and management of *Municipal Solid Waste* (MSW) are one of the major challenges facing with urban areas all over the world. Over the years, the MSW has used manifest technologies with birillant strategies. The MSW have made several attempts to reduce the environmental fire and negative impacts around the world. One of the most useful applications of the MSW are heat treatment or conversion by energy usage to get cleaner renewable sources as wastes. Among many strategies of waste to energy resources, refuse-derived fuel (RDF) is solid conversion to fuel which can be used instead of conventional fossil fuels [1]. The RDF (or Garbage Derivative Fuel is briefly named as GDF) which consist of wastes as pouch, fabric, fibre and nylon, supplied from households and industrials, cannot be recycled, reusable. The MSW with high calorific value are formed by wastes certain processes. The definition of RDF

verified by Ministry Energy Resources. The following abbreviations are used for RDF as;

- SRF - Solid Recovered Fuel
- REF – Recycled Fuel
- PPF - Paper Plastic Fuel
- PEF - Processed Engineered Fuel

The fuels are used in terms of SRF, REF, PDF, PPF and PEF, burned or combusted and dry part of urban waste, which is too dirty to be recycled [2].

The terms related to fuels with the high caloric value which were obtained from Household Solid Waste as below;

- RDF - Refuse Derived Fuel
- REF - Recovered Fuel
- SRF - Solid Recovered Fuel
- PDF - Packaging Derived Fuel
- PPF - Paper and Plastic Fraction of what
- PEF - Processed Engineered Fuel etc.

These latter, have low moisture with ash content higher thermal value compared with other mixed fuels [2].

The terms related with industrial wastes and their products (such as rubber and solvents) at a certain level with special processing steps are given below;

- TDF - Tire Derived Fuel

- SF - Secondary Fuel,
- SF - Substitute Fuel
- SLF - Substitute Liquid Fuel etc. [2].

The RDF undergoes various processes such as grinding, classification, sieving, separation of metals, reduction of samples to uniform dimensions, pelletizing and storage. The pelletizing process formed by combining small granular RDF particles structures [3]. The RDF pellets have more advantageous while compared with θ coal, whose thermal value and fuel properties are high, because they are a clean fuel, with energy efficiency, and less harmful effect on atmosphere like dust particles [4]. The RDF is a cleaner type which is more friendly to environment and has a high calorific value, which provides cheaper fuel sources, none used energy recovery compared with known fuels. And also have a high caloric value as biomass fuel. The calorific value of RDF is approximately 4100 kcal/kg [3,4]. According to the thermal values, the thermal value of Rome RDF was found to be 4895 kcal/kg, but the thermal value of Dudley urban solid waste was found to be 2388 kcal/kg [5]. The major factors of the high thermal value RDF fuel are contained such as plastic, cardboard and paper in the fuel composition. As the ratio of ingredients in the RDF, verified their thermal values [3, 4]. Only the RDF fuel can be used in energy generation systems as ovens and stoves without any other fuels. It can also be reused instead of coal as certain proportions in power plants for recycling. For example, in power plants working for waste recovery, the RDF can be used instead of coal at a ratio of 9:1 [6].

There are fuel classes and codes that can be used in RDF production due to various countries. However, as general terms, wastes that the RDF can be produced which are listed below [4].

- ✓ Domestic Solid Waste
- ✓ Industrial Waste
- ✓ Plastic and Paper/Cardboard Wastes (Outcome from Commercial and Industrial Usage)
- ✓ Packaging Waste
- ✓ Production Waste
- ✓ Waste Tires
- ✓ Biomass Waste
- ✓ Vegetable Wastes (Stalk, Straw, Shell Etc.)
- ✓ Uncontaminated Wood Waste
- ✓ Paper and Paper Production From Waste Muds
- ✓ Dried Domestic Wastewater Treatment Sludges
- ✓ Textile Wastes
- ✓ Animal Wastes
- ✓ Wastes from Vehicle Smashing or Automotive Shredder Residue (ASR)
- ✓ Hazardous Waste with High Calorific Value
- ✓ Waste Oils
- ✓ Industrial Muds
- ✓ Impregnated Wood Shavings
- ✓ Waste Solvents
- ✓ Carpet Wastes And Clippings
- ✓ Textile Waste

✓ Diaper Production Waste

An exemplary representation of MSW and RDF can be seen in Figure 2.1 [7,8].

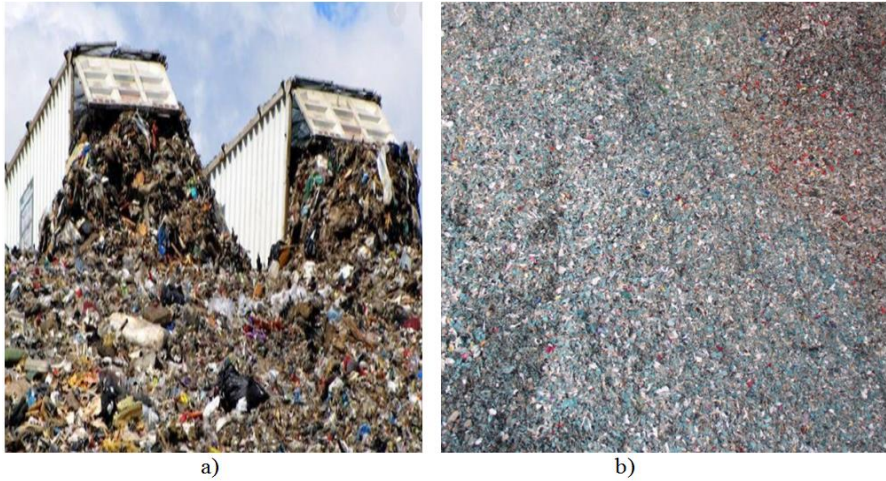


Figure 2.1. a) The (MSW) and b) The (RDF) samples [7,8]

3. RDF PRODUCTION STAGES FROM MUNICIPAL SOLID WASTE

The wastes was obtained from municipal solid wastes through different stages according to various features. These various features;

- First of all, the type of fuel that can be RDF,
- In which processes the produced RDF will be used,
- Other products that will form the fuel mixture in the process where RDF will be used,
- User demands,
- The suitability of the components in the fuel,
- It can be exemplified as under which stated the RDF, will be stored until the disposal stage after it is produced. One of the

most important factors among these examples is the disposal facility. Because it can change the physicochemical characteristics of waste such as grain size, pellet shape, ash content and moisture content [3].

Generally Municipal Solid Waste, respectively;

- Separation at source,
- Grouping by mechanical separation,
- Size reduction,
- Separation and screening,
- Mixing,
- Drying and pelletizing,
- Packaging,
- They are transformed into RDF by undergoing appropriate production processes according to demand and waste content such as storage [9]. The conversion scheme of solid wastes to RDF is given in Figure 3.1.

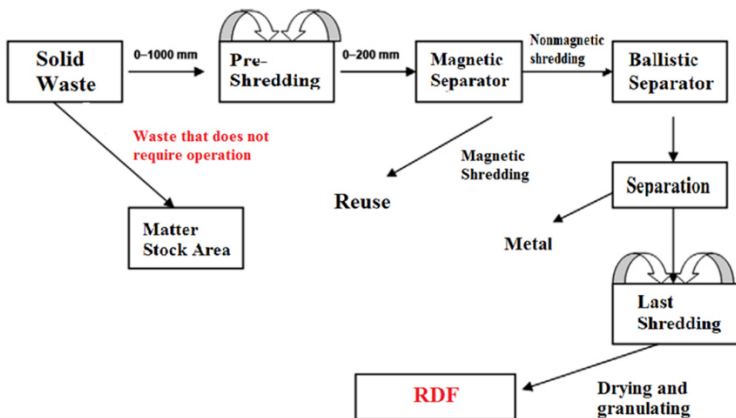


Figure 3.1. Flowchart of Solid Waste Conversion to RDF [9]

3.1 Waste Separation from Municipal Source

In this section, the wastes are graded. To achieve the desired quality level in the production of solid waste from household solid wastes, two types of process strategies are applied and named as negative or positive ratings [9].

- a. Positive Rating: It is the type of rating in which the wastes obtained by choosing harmless and non-hazardous substances with the high caloric value from the waste and generated. The amount of waste obtained by selecting this rating type and is less than the negative rating, but the fuel quality of the product output is better than others[9].
- b. Negative Rating: In this type of rating, the remaining part is used by removing the unwanted materials that make up the components of the waste. For example; Since the excessive amount of wastes in it causes corrosion in the boilers during combustion, the products containing chlorine are taken into consideration while choosing this method for the amount of chlorine that becomes a problem [9].

3.2 Grouping by Mechanical Separation

3.2.1 Separation of Ferrous Metals

Today, many different methods are used for the separation of ferrous metals. Some of these are those;

- Laying the materials to be separated longitudinally on the flow path and conveyor belt, placing a magnetic separator on the belt.

- Using a magnetic drum sorting machine or using a magnetic drum to clean small pieces of iron that cannot be discharged from the materials that need to be separated.
- To increase the belt speed in order to reduce the height of the materials to be distinguished on the conveyor belt.
- Delivery of materials that need to be distinguished in order to efficiently create mechanisms using magnetic drum sorters [4].

The usage of the magnetic sorting method in waste sorting greatly increases the quality of waste. In this method, it is generally used by placing it on the flow band along with the materials that need to be distinguished. The reason for placement throughout is the difficulty in distinguishing metal materials when placed transversely [9].

In the method of distinguishing with the magnetic drum sorter, the feeding method from above was preferred. In the magnetic drum sorting method, ferrous materials interact more with the magnetic field. The separation process takes place in a much more detailed way with this method. However, one disadvantage of this method, it is used only when ferrous metal materials are used. Based on all, it is understood that the selection of the magnetic sorting method depends on the type of materials that make up the components of the waste. The methods used vary depending on the customer request [9].

3.2.2 Separation of Non-Ferrous Metals:

Eddy current sorter is a method used for the removal of non-ferrous metals. In order to use this method, certain operations must be done before hand. Increasing the particle size to certain dimensions (3mm-

150mm), it is among these processes. Besides, the high-frequency magnetic field is used in order to eliminate the thinner metals from the waste that it needs to be distinguished. Apart from this method, vibrating grooves that form a single particle layer can be used as a better sorting system [9].

3.3 Rotary Screens

The general structure of the rotary screens, which are especially used in the treatment of domestic waste, is in the form of a cylindrical drum. With this method, separation is made according to the size of the waste [4]. The types of sieves commonly used in the method are given in Figure 3.2.

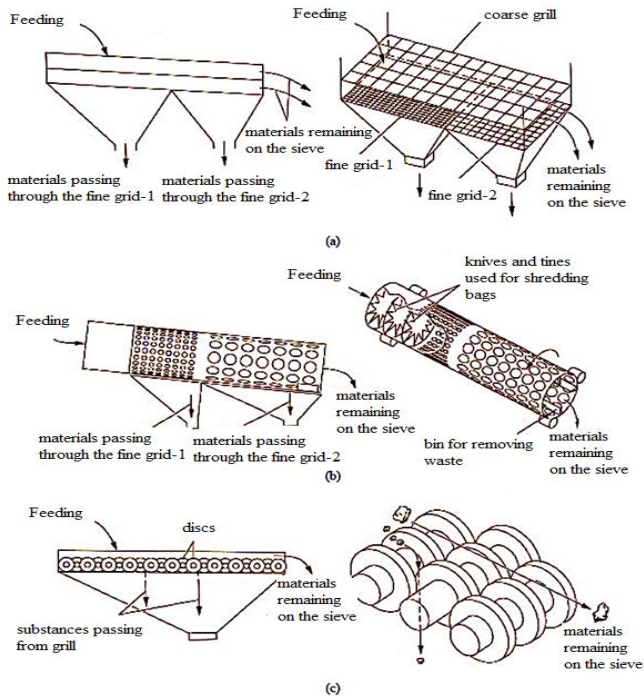


Figure 3.2. Commonly used sieves a) Vibrating screen b) Rotary screen c) Disc screen [10]

With the rotary drum sieve method, the materials of certain sizes pass under the screen as a result of the rotational movement of the drums, allowing the large and small grains to be distinguished. One of the advantages of the method, depending on the rotating speed of the rotating drum, it can be created in different working conditions. Cascade and gradual mode forms of these working conditions can be given in Figure 3.3. [9,10].

When rotating screens are working in a graded mode, the critical rotation speed can be seen about 70%. This speed is considered as the most productive time of working conditions. However, the disadvantage of the gradual mode is the obstruction of the eyes on the sieve as a result of loading materials to be distinguished on average of 250 mm. In addition, as a result of this clogging, it is very difficult to remove fine materials and tubers. In order to solve problems that occur and increase the working efficiency, apparatus that will enable materials in the rotary screen to be carried up and developed. It was observed that these apparatuses developed increased efficiency as a result of the trials [9,12]. Rotary drum sieves and their positions are given in Figure 3.3.

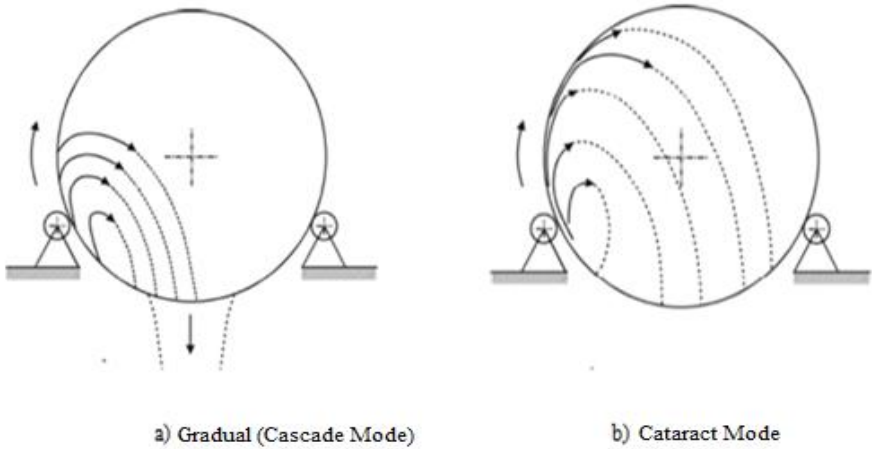


Figure 3.3. Rotary drum screens and their positions [9,11]

3.4. Near Infrared Spectroscopy (NIR)

Material sorting is generally done with the assist of conveyor belts. Sensor sensors and lamps are placed on the upper part of the conveyor belts used. Near Infrared Spectrometry (NIR) is available at the top of these sensors placed on the tape. The sensors scan the entire band across its width and width and transfer the characteristic spectra of the components that make up the waste to the processor. These transferred signals are compared with the database. In this process, measurements result even before seconds pass. The grading process is started by using air spray nozzles after these processes. Generally, this method is used to separate some unwanted components in the waste that will become fuel. The disadvantage of the method is that dark brown and black materials in the waste are not distinguishable. The reason for this disadvantage is that the black material absorbs all of the light of the spectroscopy. As a result of the black or brown materials

swallowing the light, it cannot be reflected and data transfer cannot be provided. In general, this method is preferred when chlorine content and heavy metal amount need to be reduced. Considering the standards, other materials such as PVC material that do not have waste should not have more than 3% chlorine content [9]. In some circumstances, this rate may decrease to 1%. Municipal solid wastes before and after separation are given in Figure 3.4.



Figure 3.4. Municipal solid wastes before and after separation [12]

3.5. Automatic Collection and Sorting

In this method, wastes are continuously fed on the conveyor belt using vibrating grooves. Metal detector sensors are placed on top of this conveyor belt. These installed sensors transfer individual data of the wastes flowing over the conveyor belt to the computer. Along with these sensors, a color camera is placed on the upper part of the conveyor belt. This color camera collects the data of the materials flowing through the tape and transfers it to the computer. All the information flows created are analyzed using improved software.

From these analyzes, implants are sent to the nozzles and unwanted waste pieces are exported with the positive and negative rating method. These unwanted wastes transferred and separated wastes are stored on different bands or sent to the desired center. The waste sizes, used in the method, vary between 3-250 mm [9].

3.6. Drying

Waste drying process means the amount of excess moisture in the waste (water amount) reduction is called the process. During the drying process, there is no change in the chemical structure of the materials in the waste characterization. The drying process can be done with many different methods today. The most well known of these methods are;

- **Using Heat to Perform Drying:** Moisture amount is removed from the heater using a heating medium in this method. It is examined under two titles as heat diffusion and heat transfer. Direct contact takes place between the waste and the heating medium in order to reduce the moisture content of the waste in the heat-dissipating dryer types. In heat-permeable dryers, there is no contact between waste and heating medium in order to reduce the amount of moisture in the waste. This method is generally preferred for dust and odor containing wastes [9].
- **Biological drying method:** The main purpose of the biological drying method is the method of removing heat and moisture in order to enable mechanical separation of the parts that make up the waste characterization more easily and efficiently [9]. The

flow chart of the biological drying scheme is given in Figure 3.5.

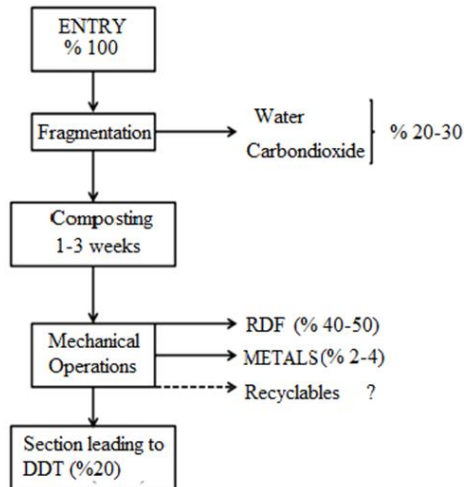


Figure 3.5. Flow chart of the biological drying system [13]

In this system, the mechanical separation of wastes is done after biological treatment. In the bio-drying process, waste is first broken down. After the waste shredding process is completed, the wastes are taken to the bio-drying tank. In this method, it is necessary to provide the necessary conditions for the production of heat by the microbiological working method. For this reason, it is desired that air be fully penetrated the waste. The generated heat is expected to evaporate the water in the waste and to dry the waste with this method. However, the point to be considered here is that water is also needed for the microbiological study, so the amount of water in the waste should be on the order of 15-20%. In this method, additional drying is done. In the additional drying process, the air is fed to the system by applying preheating by passing it through the heat

exchanger. A reduction in the amount of dirty air is created by reusing the airflow through the reverse flow in the process.

With these methods, as a result of drying the waste, the calorific value of the waste is increased [14]. Bio-drying elements are shown in Figure 3.6.

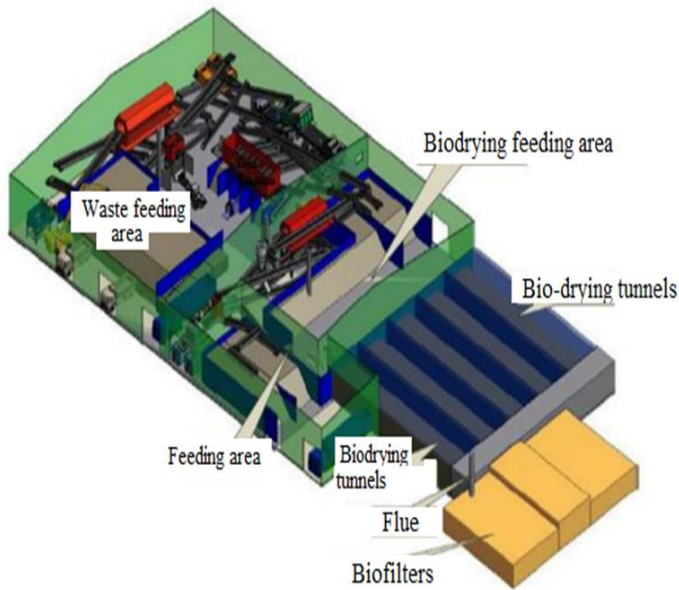


Figure 3.6. Bio-Drying Elements [15,16]

3.7. Granulating

In this method, disc flocculants are used to take the form of waste and granules. The disks on the clumps are designed and manufactured specially in order to mix the wastes better. As a result of the rotational movement of these discs, a heat caused by friction occurs. In other words, while the waste is mixed in this method, it also starts to melt due to the heat generated by friction. While the process is continuing, after the waste starts to melt, it is now transition to plasticization.

Energy consumption increases at the time of this transition and after. With the increase, signals are sent because the container in which the waste now needs to be emptied. During these processes, while the heated materials are discharged from the containers, they are brought to the desired granule size with the necessary equipment. It is left to cool afterwards. This method is generally used for waste characterization in wastes with components such as plastics that can melt [7]. An example representation of the RDF prepared according to the part size is given in Figure 3.7.



Figure 3.7. RDF ready by part size [14]

3.8. RDF Production Facility Different Technologies

In the selection of equipment to be used in the RDF production facility, attention should be paid to the provision of equipment capable of handling waste. In other words, the capacity, technical features, brand and model equipment prices of the selected equipment are

important to us. These factors affect both the quality of waste and the cost of the facility, and the equipment can be varied or increased in number/capacity for these reasons. Under this title; from mixed domestic solid waste (Figure 3.8.), mixed and moist solid waste without organic waste (Figure 3.9.), mixed solid waste without organic waste (Figure 3.10.), uniform waste (Figure 3.11), single waste free from bulky waste General flow charts of RDF productions from type waste (Figure 3.12.) are shown [9,17].

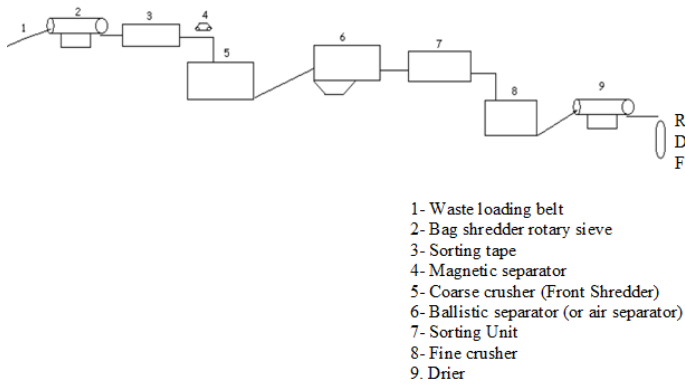


Figure 3.8. General flow chart of mixed domestic solid waste plant for RDF production [9]

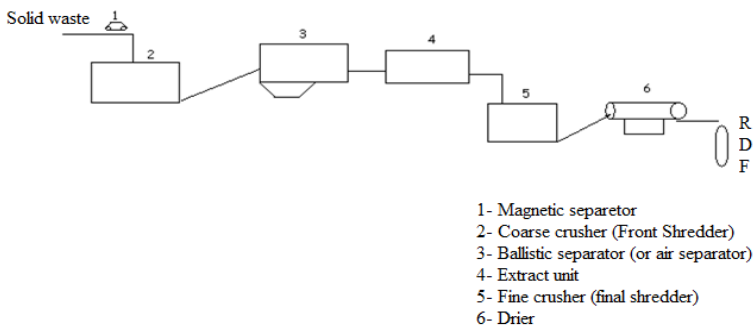


Figure 3.9. RDF production from mixed and moist solid wastes without organic waste [9]

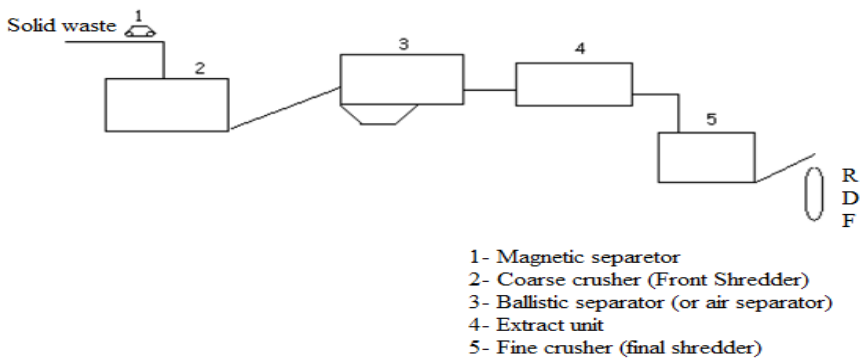


Figure 3.10. Production of RDF which does not require drying from mixed solid wastes without organic waste [9]

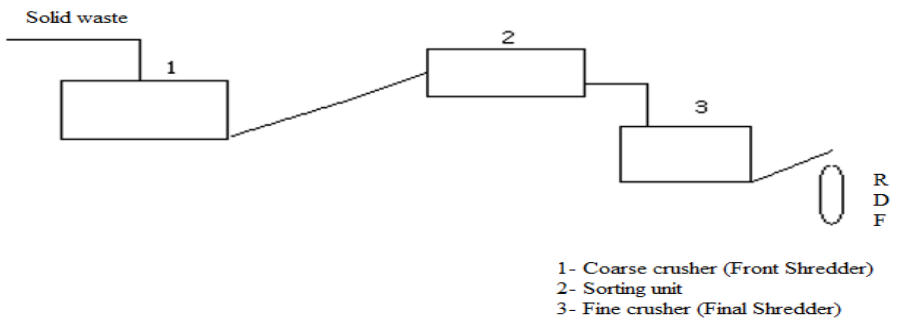


Figure 3.11. RDF production from uniform waste (no drying required) [9]

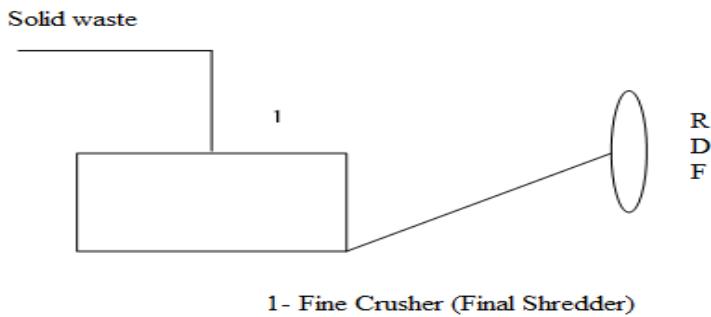


Figure 3.12. RDF production from a uniform waste-free waste [9]

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CHAPTER 2
**WASTE DESCRIPTION, CLASSIFICATION AND SEPARATE
COLLECTION ON SOURCE**

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1. INTRODUCTION

The problem of environmental pollution, which increases as a result of wastes, developing technology and industrialization as a result of human activities, is increasing day by day. This increase in waste endangers the lives of people and other living creatures around the world [1]. Various methods have been developed in order to reduce this increasing problem regarding waste. At the same time, he encouraged individuals working in this field to conduct studies to examine new fuel potentials that may occur from these wastes and new concepts emerged. With these concepts, important results were obtained in terms of waste and fuel, such as increasing the quality of fuel and reducing the volume of waste.

2. DESCRIPTION AND CLASSIFICATION OF WASTE

Waste is a by-product of human activities; it is a low value, non-use product and useless residue. Among the wastes; the waste material that remains after the separation of materials such as paper, glass, cardboard, plastic and which cannot be used in any way is called garbage. Solid waste and purification sludge, which are intended to be disposed of by the producer and that need to be disposed of regularly, especially in terms of the protection of the society and the environment, are called solid waste. [1,2]. On the condition of not being imported; In addition to urban wastes, including vegetable oil wastes, agricultural harvest wastes; The resources obtained from agricultural and forest products and by-products resulting from the processing of these products and waste tires, and industrial sludge and

treatment sludge are called biomass [2,3]. Wastes: They are classified according to different criteria such as physical condition, original use, physical properties, source and level of safety. The classification of solid wastes according to their source is given in Figure 1.1.



Figure 1.1. Classification of solid wastes by source

1.1. Medical Waste

The wastes obtained from health sectors such as health centers, hospitals, pharmacies and drug use, surgery or treatment methods are medical wastes. Medical wastes are special wastes that must be collected separately from domestic wastes and properly disposed of. In our country, medical wastes are managed within the framework of the “Regulation on Control of Medical Wastes” published in the Official Gazette dated 22/07/2005 and numbered 25883 [4]. World health organization to medical waste; He made various classifications as infectious, chemical, heavy metal, pressure vessel, radioactive, pathological, cutter-piercing and pharmaceutical waste. It is very important to classify such hazardous wastes by classifying them and then it is very important to be disposed of consciously. Otherwise, they can create many irreversible problems. The vast majority of disposal methods for medical waste are the same as for municipal solid waste disposal methods. In other words, approximately 80% of

medical waste can be disposed of by municipal solid waste removal methods, while the remaining 20% must be disposed of different methods. To summarize, these disposal methods also change according to factors such as the type of waste, the environment in which it is available, and technology. The important thing is to make this disposal most correctly [5]. In Figure 1.2, there is an example representation of medical wastes.



Figure 1.2. Medical wastes [6]

1.2. Hazardous Waste

No harmful, burning, poisonous, explosive, oxidizing, carcinogenic, corrosive, mutagenic, infectious, ecotoxide in their physical and chemical properties that may harm human health and nature arising from different production facilities and industrial establishments, requiring special processes in the process of removal from the all harmful and hazardous wastes resulting from interacting with any substance or substance are called [7]. To summarize, industrial and

domestic solid wastes containing substances considered to be harmful and dangerous for the health of living creatures in the environment and nature are called hazardous wastes [8]. For example battery, various chemicals, battery etc. Hazardous wastes are classified in two different ways: content and source [9]. There are some points to consider when deciding whether a waste is a hazardous waste. These are the components that make up the waste and the quantities of these components, chemical reactivity, and the effects of the waste on the environment and its permanence and physical condition. Because it can cause chemical reactions by being affected by the environment in hazardous wastes with their components. As a result of the chemical reactions that occur, they can create substances that damage the environment and living things [8]. An example of hazardous waste is given in Figure 1.3.



Figure 1.3. Hazardous waste [10]

1.3 Construction Waste

Construction wastes are called wastes caused by repairs, renovations, demolitions and natural disasters of buildings such as bridges, roads and residences. The variety of these wastes varies according to many factors such as construction technique selection and type of materials used. We can list a few of these wastes in the form of concrete, plaster, brick, briquette, wood, glass, metal piece (steel aluminum, copper, brass) gypsum plasterboard, tile, plastic, electrical materials, pipes and asphalt. When the regional profile of construction wastes is examined, it is seen that the waste characterization changes. Construction wastes account for approximately 13-30% of urban solid wastes [11]. If these construction wastes are not taken under control, they may pose risks that may harm the environment, human beings and other living creatures and speed up ecological destruction. In addition, the fact that construction wastes are not correctly evaluated and not controlled can cause great damage to the economy [12]. For example, the construction industry contributes approximately 9.8% of the economy of the European Union. With the correct disposal, this ratio can be achieved or even increased in every region. One of the disadvantages of construction waste is that the volume of waste is large compared to other types of fuel, such as domestic, medical and hazardous waste [13]. For these reasons, construction waste has an important place among the wastes that need to be disposed of very well. In Figure 1.4, there is an example representation of construction wastes.



Figure 1.4. Construction waste [14]

1.4. Industrial Waste

Solid wastes that occur during industrial and production processes and are separated from hazardous and harmful substances. Briefly, wastes generated during or as a result of industrial processes are called industrial wastes. These wastes are generally machine parts that have reached the end of their life or materials with production residue [15,16]. Industrial wastes can be analyzed under the three different headings for their formation factors. These; solid wastes from processes and processes in industrial units are industrial wastewater treatment plant sludges and solid wastes from air pollution control equipment. Before the industrial wastes are separated, there are hazardous wastes formed as a result of the processes and processes in the industrial units. These wastes are defined as harmful solid wastes.

This issue has been discussed above under the heading of hazardous waste [17]. The industrial waste can have dangerous consequences for humans, the environment and other living things. In order to prevent these damages, these wastes must be destroyed, recycled or recycled [18]. Reuse of industrial solid waste is available in many areas. Concrete technology, highways and the automotive industry are some of these areas [19,20,21]. There is an example of industrial wastes in Figure 1.5.



Figure 1.5. Industrial waste [22]

1.5. Domestic Waste (Municipal solid waste)

Wastes that do not contain any hazardous substances in workplaces, residences, and commercial activities are called domestic wastes. For example; water, etc. plastic bottles, packaging packages, tin, cardboard, paper, metals, garden waste etc. There are various names for these wastes such as solid waste or municipal solid waste. The

progressive development of city centers and population growth cause urban solid waste to increase [23]. Increasing domestic wastes endanger both the environment and the health of living things, although not as much as medical and hazardous wastes. With increasing urban wastes, the volume of waste has increased, field problems have arisen, environmental pollution has arisen, and there have been some difficulties in management in its disposal [24, 25]. At the same time, the random disposal of wastes by our citizens has led to an unhealthy life. In other words, the harms of domestic wastes are related not only to their proper disposal but also to the low environmental sensitivity of humans [26]. Due to all these negativities, solid wastes must be disposed of in a way that will cause the least harm to the environment and living life. Today, the most suitable form of disposal for this purpose is recycling with high economic value in the waste [25]. In Figure 1.6, there is an example representation of domestic waste.



Figure 1.6. Domestic waste (Municipal solid waste) [27]

The factors affecting this rapidly increasing waste generation and the diversity of its components are the socio-economic structure, geographical location, energy resources and climate changes of the settlement. In addition, the income level factor of the regions that are at the top of all these factors should not be forgotten. Significant differences were observed in the content of municipal solid wastes, depending on the level of income. These differences are clearly shown in Figure 1.7. [28, 29].

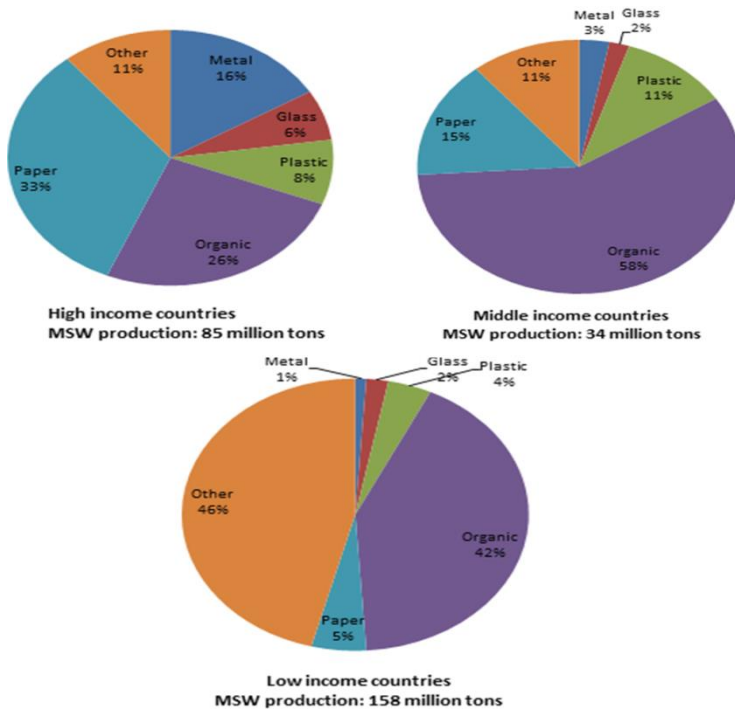


Figure 1.7. Change in the municipal solid waste component of countries depending on income level [28,29]

The main waste component of the category described as other in low-income countries, which is also seen in Figure 1.7. This amount of ash is four times higher than in countries with high and middle-income

levels. However, the amount of compostable organic matter for middle and low-income countries is quite high compared to high-income countries. The recyclable part of the waste is seen to be quite low in low-income countries. The main waste component of the category described as other in low-income countries, which is also seen in Figure 1.7. This amount of ash is four times higher than in countries with high and middle-income levels. However, the amount of compostable organic matter for middle and low income countries is quite high compared to high-income countries. The recyclable part of the waste is seen to be quite low in low-income countries[28,29].

2. SEPARATE COLLECTION OF WASTE

The process of separating wastes according to their types in waste collection centers is called separate collection at the source of waste. Wastes;

- Reuse,
- Regain,
- They can be evaluated in three different ways: recycling.

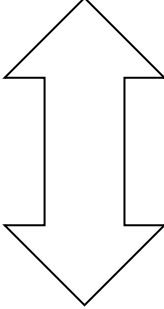
These steps are explained one by one below.

2.1. Reuse

It is the reuse of the wastes obtained without any chemical change in their chemical structure. In other words, the reuse of waste without re-collecting and cleaning is used economically over and over until the end of its economic life. Glass bottles can be cleaned and used

repeatedly and water bottles used as water bottles are examples of reuse [30]. It is ranked second in the reuse waste management hierarchy. Linear optimization methods used in order to design solid waste management have been used for the reclamation and recovery of waste, if possible. In the past, wastes were collected, transported and buried in the soil according to traditional methods known at that time. These methods, which we call wild storage, are still used randomly even today. As a result of this indiscriminate wild storage, great damage to the air, soil and living health is caused. It does not only harm but also creates fires and ends the lives of many living things. Fortunately, wastes are classified at the source, collected, processed and disposed of by appropriate methods, with new methods developed nowadays. If there are wastes that cannot be disposed of even with energy recovery methods, they are buried as the last resort. [31,32].When the hierarchy is examined carefully, it is the most preferred prevention of waste generation. However, the most preferred method after waste emerges is the reuse of waste. If these are not possible, go to the lower options. In other words, the importance and place of reuse in the waste hierarchy are great [33]. Waste management hierarchy is given in Table 1.1.

Table 1.1. Waste management hierarchy [34]

The most preferred	Prevention
	Decrease
	Reuse
	Recycling
	Energy Recovery
Least preferred	Throwing in the trash

2. 2. Regain

It is the conversion of the waste to a substance with similar or the same through various mechanical processes. For example; Processing like paper can be used again as paper. We act for some purposes in the recovery of waste. These objectives are; resource protection, environmental protection, energy-saving and space-saving. The purpose of resource conservation is to use idle waste as secondary raw material. In doing so, we reduce the consumption of primary raw materials. The purpose of environmental protection is to reduce the pollution of water, air, soil and visual pollution, which is harmful to the environment by recyclable wastes. The purpose of energy recovery is to use the energy content bypassing waste materials through various systems such as incineration and gasification, thus reducing their consumption rate by supporting renewable energy sources. The

purpose of saving space is to provide longer-term use of regular storage areas by separating and reusing fuels that can be recycled. All of these values and purposes, Turkey has occurred as deemed appropriate recycling quotas by the Ministry of Environment [35].

2.3. Recycling

It is the process of converting wastes that can be utilized through various physical and chemical processes into a new product or raw material. For example; yarn, nylon production, etc. from pet bottles. The recycling process consists of pre-collected, reproduced and re-used stages [36]. In other words, to define recycling, if new parts are to be produced from raw material, it is to convert the parts used and the parts that make it into a product [37]. While recycling, the amount of waste is processed through incineration, recharging or burial. After these processes, a decrease in the amount of waste occurs. This decrease contributes to the economy and our need for raw materials, as well as saving energy [38]. In Figure 1.8, the separation process scheme of municipal solid waste is given.

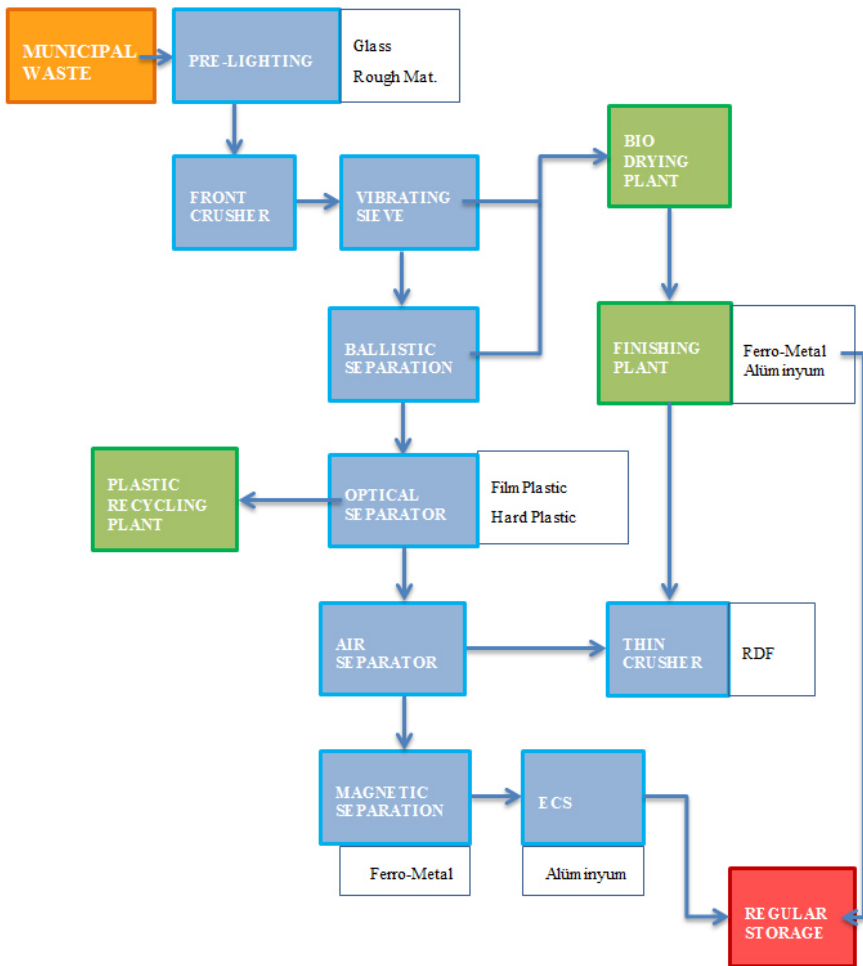


Figure 1.8. Municipal solid waste separation process scheme [39]

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CHAPTER 3
GREEN STATE OF WASTE TO ENERGY AS FUEL OF
BIOGAS: TURKEY CASE STUDY

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1. INTRODUCTION

Worldwide energy has required increasing each moment while by the waste of human rise. Thus, mainly, energy has to suspend by recycling of waste which can be produced from foods dispose of, electronics, tire and uncountable of waste products. The waste material much increases due to great human population and essentially industrialization [1]. Thus, energy or heat has been utilized by thermochemical, physicochemical and biochemical processes which shown in Figure 1. The crucial of waste classified into municipal, dried sewage sludge, agricultural, medical, e-waste, and building wastes [2]. According to crucial of wastes, municipal dispose of significantly contain paper, food waste, wood and yard trimmings, cotton, glass, metals and plastics [3]. Generally, waste problems have been resolved through landfilling and incineration. However, uncontrolled various gaseous were output to nature which cause health problems and death of animals and plants. As a result of the waste problem, alternative methods have to use to control emission gas (such as biogas) in a useful form. Therefore, Biochemical Conversion of Anaerobic Digestion (AD) method used to produce biogases where raw materials can be supplied from the waste of food and also the waste of animals as rich gases products.

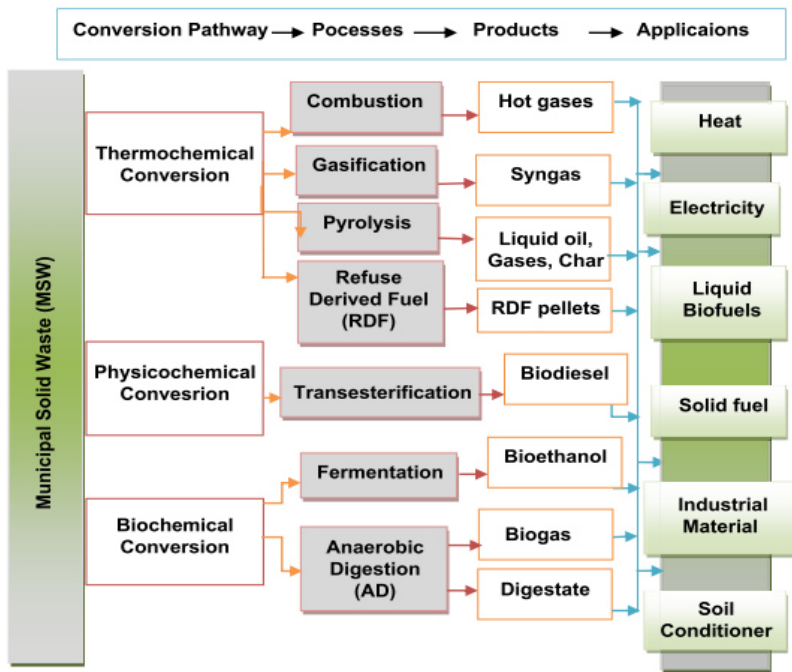


Figure 1. WtE based on conversion techniques [4].

Biogas Plants have given static and dynamic action at founded zone. The dynamic effects are a long time utilization with the increase in income and decrease unemployment. And also, static actions are a short time foundation with high investment. In this significant point, wastes have to recycle by novel methods for future green fuel as biogas [5].

2. BIOGAS PROPERTIES AND PRODUCTION STEPS

Fuel production with biogas biotechnology is an important alternative method. In recent years, industrial, plant waste, domestic waste, animal waste and human-sourced waste and solid waste (garbage)

have been used to recycle [6]. In Turkey, 65% of the total waste form as organic waste. This shows that it is a great source for biogas [7].

The latte raw materials turn into methane gas in the reactor in an oxygen-free environment medium. The refusal waste of reactor can be used as fertilizer. Biogas which is colorless, flammable, its main components is methane and carbon dioxide, and it contains hydrogen sulfide, nitrogen, oxygen and carbon monoxide as trace compounds. The organic raw material is transformed into biogas with a ratio of 40% and a maximum of 60%. The natural gas and biogas samples were compared in Table 1. As can be seen from the table, in particular, methane gas amount is 55-70% in biogas, while in natural gas as 92%. Especially, the thermal value of natural gas is 48.4 MJ/kg, and biogas as 20.2 MJ/kg [8].

Table 1. Natural Gas and Biogas Ingredients [8].

Parameters	Natural Gas	Biogas
Methane (%)	92.0	55-70
Ethane (%)	5.1	0
Propane (%)	1.8	0
Butane (%)	0.9	0
Pentane (%)	0.3	0
CO ₂ (%)	0.61	32-45
N ₂ (%)	0.32	0-2
H ₂ S (mg/m ³)	1	0-15.000
NH ₃ (mg/m ³)	0	0-450
Net Calorific Value (MJ/kg)	48.4	20.2
Density (kg/Nm ³)	0.809	1.16
Wobbe Index (W)	54.8	27.3

A complex biochemical reaction takes place by microorganisms (acid and methane bacteria). The organic substances were consumed by bacteria as follow:

- Acid Bacteria which produce acetic acid with butyric/propionic acid
- Methane Bacteria who use hydrogen with acetic acid

Biochemical reactions, shown in Figure 2, take place in three steps [9,10]:

- Hydrolysis,
- Acid production,
- Methane production,

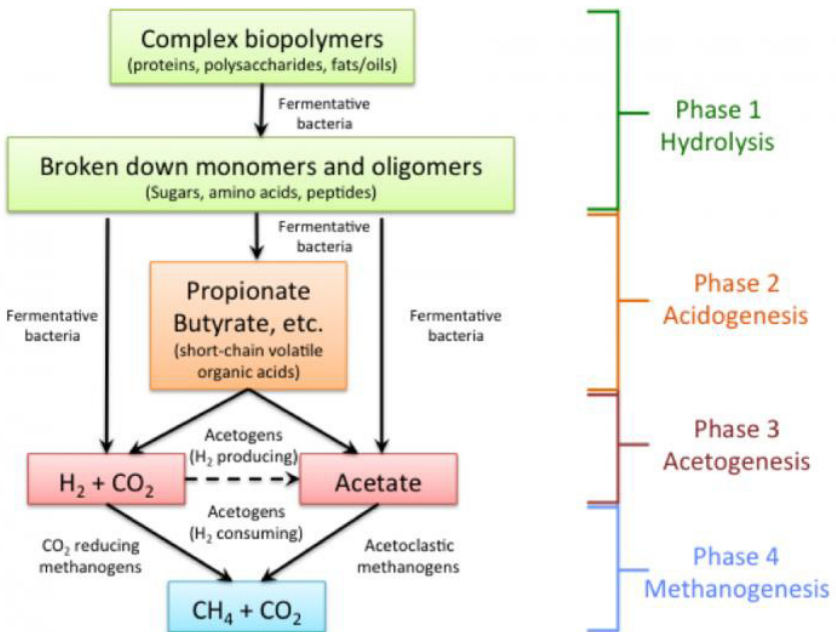
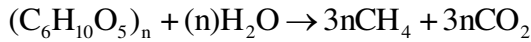


Figure 2. Biogas Production Steps [11]

2.1. Hydrolysis

Hydrolysis is a conversion of polymers into monomers. On the other hands, hydrolysis takes place with the extracellular enzymes of solid and dissolved heavy organic bacteria in an airless environment and turns into a lower weight organic molecule. Hydrolysis is a slow reaction rate affected by pH, temperature and sludge age (dwell time). Total anaerobic fermentation was reacted by polysaccharides of the polymer of glucose by hydrolysis [12].



2.2. Acid Production

The methane is formed by the conversion of volatile fatty acids into acetic acid and then depolymerize of acetic acid or the interaction of carbon dioxide and hydrogen. Bacteria formed acetic acid transformation into dissolved organic compounds as smaller monomer structures. The bacteria can also be called as anaerobic. They create an anaerobic medium to produce methane. If the acidic ratio is more than 1000-1500 mg HAC/L, the pH value drops. So, methane bacteria are exposed by the inhibition effect.

For acid production stability satisfied by as propionic, butyric, isobutyric, valeric and isovaleric acids.

The fatty acids convert into more than two carbons structure by acidic reactions. At the first level of fermentation or acidogenic bacteria used to convert hydrolysis products into oligomers and monomers organic acids and solvents. Some types of acidogenic bacteria (homoacetic

bacteria) produce acetic acid by using carbohydrates. Some of them also produce hydrogen.

Finally, hydrogen and carbon dioxide react to produce acetic acid and water [8].

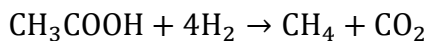
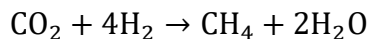


2.3. Methane Production

Anaerobic fermentation was occurred by bacteria of methane which can be classified into 3 groups as:

- Psikofilic bacteria: 5-25 °C
- Mezofilic bacteria: 25-38 °C
- Termofilic bacteria: 50-60 °C

Psikofilic bacteria live at deepest local of sea and lake, termofilic bacteria live at the geothermal marsh and volcanic local [13]. Methane is produced by acidic depolymerization with hydrogen and carbon dioxide synthesis [14].



3. BIOGAS PRODUCTION PARAMETERS

3.1. Feeding Frequency

To keep the solid substance amount as constant in the reactor, it has to feed regularly. This situation increases the rate of decomposition of organic matter as gas production increases. The daily feeding amount

is calculated by dividing the volume produced by the holding time [15].

$$\text{Daily Feeding Amount (l/day)} = \text{Production Volume (l)} / \text{Holding Time (day)}$$

3.2. Solid Amount

Optimum methane production occurs when the solid matter content used in biogas production is around 7-12%. If the solid matter is too big while the mixing process is difficult but the biogas yield cause to decrease. On the contrary, biogas decreases again when the bacteria smash at organic matter medium [16].

3.3. Hydraulic Holding Duration

Hydraulic Holding Duration (HHD) is the production of biogas by the bacteria which decaying organic materials. It is found by the ratio of reactor volume to daily flow rate as below equation. In the biochemical reaction, %70-80 of the raw material put into the reactor, the HHD increases from at least 20 days to 120 days; depending on the climatic conditions. If there is not enough HHD, the amount of biogas production decreases because enough bacteria do not reduce the fatty acid ratio for fermentation. While the temperature of HHD decreases during reaction which increases the amount of biogas [17].

$$\text{Hydraulic Holding Duration (HHD)} = \text{Reactor Volume (m}^3\text{)} / \text{Daily Flow Rate (l)}$$

3.4. Organic Loading Speed

The daily organic loading rate is defined by the amount of organic material.

Organic loading rate for anaerobic treatment ($\text{kg}/\text{m}^3\text{-day}$),

VSC: Volatile Solids Concentration, kg/m^3

Q: Daily flow rate, m^3/day

V: volume of liquid, m^3

Under mesophilic operating conditions occur when acid ratio decrease and pH decreases. In this case, it affects the function of bacteria reaction. Due to the situation, the rate of biogas production is low at this medium [17].

$$\text{Optimum Reaction Medium} = \frac{Q \times \text{VSC}}{V} = \frac{\text{VSC}}{\text{HHD}}$$

3.5. Mixing Speed

One of the most critical parameters in the anaerobic digestion process is the mixing speed. To create a homogeneous heat distribution in the reactor, mixing speed plays an important role in reducing solid matter while allowing bacteria to react properly. Mechanical mixing can be done well at biogas recycle or sludge recycles. By mixing speed; gas is discharged from the reactor as well as precipitation and foam is prevented. Furthermore, the formations of dead zones reduce and prevent the digester volume (Figure 3) [18].

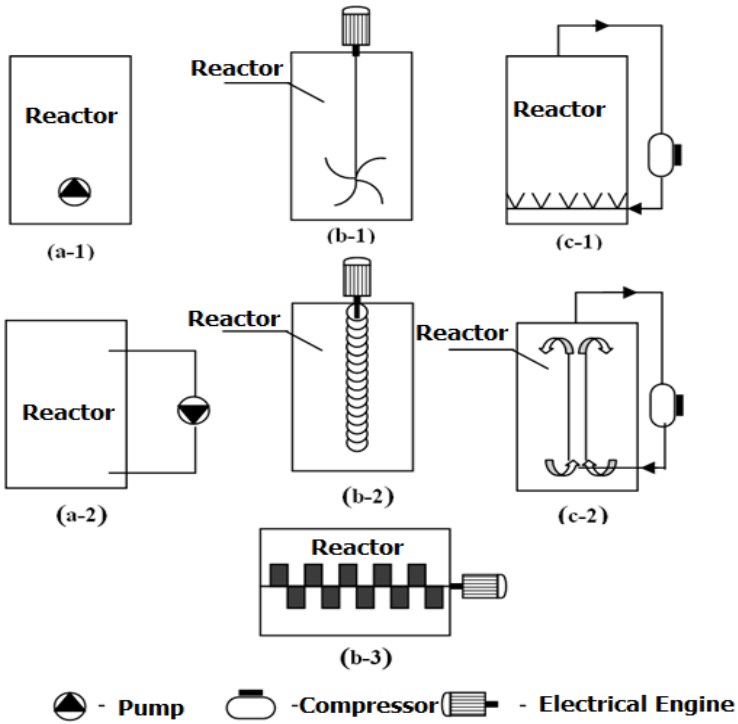


Figure 3. Mixing systems [19]:

- a) Hydraulic mixing systems: 1) with internal pump 2) with the external pump
- b) Mechanical mixing systems: 1) Propeller 2) Screw 3) Crawler
- c) Biogas mixing systems: 1) Mixing with biogas diffusion 2) Mixing with the buoyant force of biogas

3.6. Temperature Control

One of the most important parameters affecting the fermentation yield is temperature. Psychrophiles, Mesophiles and Thermophiles temperature ranges are allowed by bacteria to grow and produce biogas, shown in Figure 4 and Table 2. The tolerance of each temperature range is ± 2 , ± 1 , ± 0.5 °C/h, respectively. Optimum temperature is provided by solar energy, heat exchangers and some environmental conditions [20].

Table 2. Temperature ranges and waiting times [21]

Bacteria Types	Reaction Temperature Range (°C)	Minimum Holding Duration (Day)	Optimum Temperature (°C)
Psychrophiles	<20	70-80	17
Mesophiles	30-42	30-40	37
Thermophiles	43-55	15-20	48

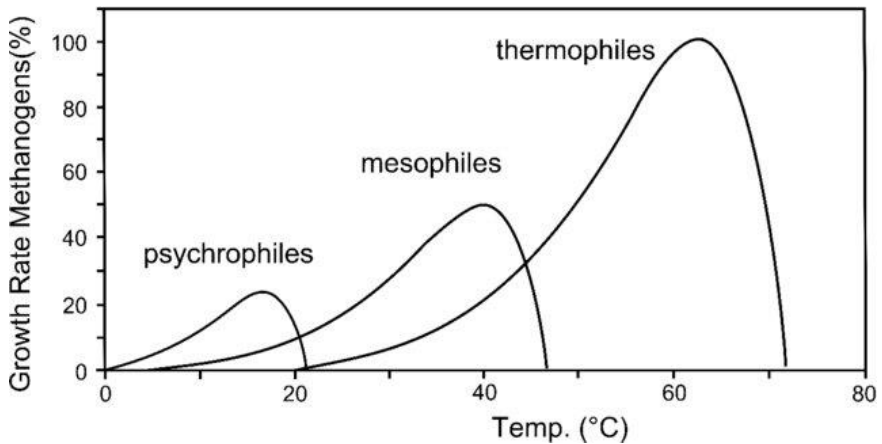


Figure 4. Bacteria growth speed due to temperature change [22]

3.7. pH Control

The methane gas is produced by microorganisms at a pH value of 7-7.5 or neutral or slightly alkaline. The pH control is kept in balance between 7-7.5 at carbon dioxide or bicarbonate or ammonia-ammonium medium (Figure 5). If the pH drops below 7, bacteria will have a toxic effect. Therefore, calcium hydroxide and sodium bicarbonate can be fed into the reactor to increase pH value [23].

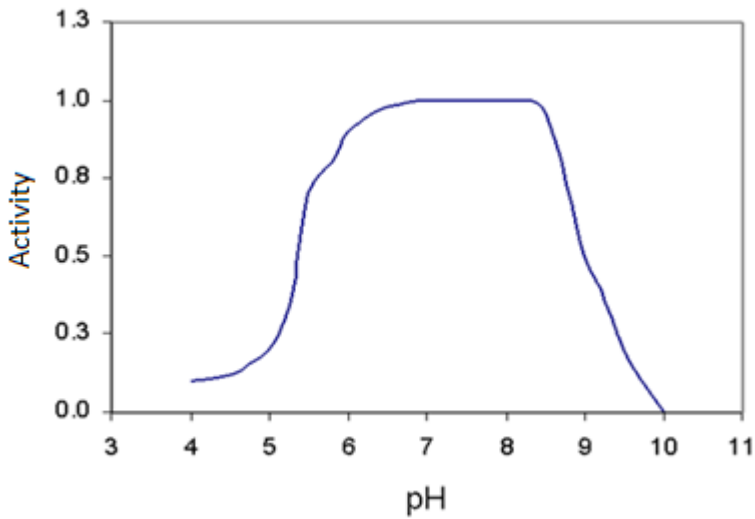


Figure 5. Various pH values for methane bacteria production [23]

3.8. C/N Ratio

In all organic materials, such as; nutrients, animal fertilizers, and human waste contain carbon, nitrogen and oxygen elements. The carbon is a basic requirement element to anaerobic bacteria for the production of biogas. And nitrogen and phosphorus are other important elements. Nitrogen enables them to grow and reproduce microorganism. It balances the pH by balancing the volatile fatty acids of nitrogen which transformed into ammonia and for the synthesis of amino acids, proteins and nucleic acids. The C/N ratio is required to react in the reactor at optimum conditions [16].

3.9. Foam Formation and Control

Foam formation is minimized by increasing temperature or sludge holding duration. The gas bubbles suck into the sludge particles or during gas separation, the foam occurred. The rate of breakage also

increases when biogas appears. It increases by an increase in oil concentration or a decrease in pH or a shorter waiting time. As a solution, water spray to foam by extinguisher or reduced by mechanical mixing [24].

3.10. Inhibit Elements

Ions, heavy metals and detergents ensure the formation of toxic and prevent the growth of bacteria. While ions at the trace level enable to develop microorganisms and prevent heavy metals. The optimum values for bacteria are presented in Table 3 [11].

Table 3. Inhibit Elements for bacteria growth [8].

Inhibit Elements	Inhibit Levels (mg/l)
Sulphate (SO ₄ ⁻²)	5,000
Sodium Chloride (NaCl)	40,000
Nitrate	0,05
Copper (Cu ⁺²)	100
Chrome (Cr ⁺³)	200
Nickel (Ni ⁺¹)	200-500
Sodium (Na ⁺¹)	3,500-5,500
Potassium (K ⁺¹)	2,500-4,500
Calcium (Ca ⁺²)	2,500-4,500
Magnesium (Mg ⁺²)	1,000-1,500

3.11. Pressure

The pressure is generated in the reactor which is affected by microorganisms. Thus, it effects to increase or decrease the efficiency

of the reaction. In a general manner, maximum biogas is obtained at ideal pressures, between 0.75 and 1.5 kPa [25].

As a conclusion: biogas is obtained due to latte conditions for the optimum or maximum amount of gas product or others. Biogas compositions are arranged between CH₄ (%55-75), CO₂ (%25-45), H₂ (%1-10), N₂ (%0-0.3) and H₂S (%0-3) [26]. Thus, optimum anaerobic conditions were declared in Table 4.

Table 4. Optimum Anaerobic Conditions [26]

Parameters	Optimum Conditions
Waste Compositions	C, N, P, O ₂ , NO ₃ , H ₂ O ₂ , SO ₄ , other trace elements
KOI/N/P	300/5/1
pH	6.5-8.2
Temperatures	25-40 °C (Optimum 35-37 °C) or 50-60 °C (Optimum 55 °C)

4. BIOGAS FERMENTATION

4.1. Feed (Batch) Fermentation

Biogas is produced by collecting at fermenter or production tank system with animal or plant wastes due to changing the holding time and temperature. After the system is completely cleaned from waste materials, then waste material are filled again by raw materials (Figure 6) [27].

4.2. Feed-Batch Fermentation

The fermenter is filled with a certain amount of waste material and fed with organic material for the production of biogas in each biogas production. After the reaction is finished, system clean and feed again (Figure 6) [27].

4.3. Continuous Fermentation

Biogas is produced every day after certain amounts of waste is added and hold. Organic material is given to the fermenter in certain amounts every day, kept for the retention period and the fermented material in the same proportions is taken to the fermenter tank daily. Thus, continuous biogas production is provided by daily feedings materials (Figure 6) [27].

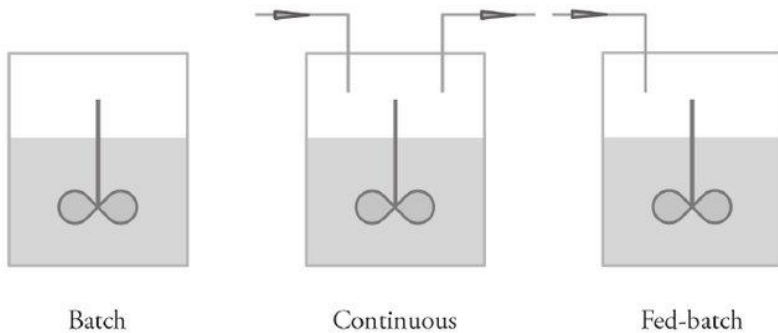


Figure 6. Fermentation types [27]

5. TREATMENT OF POLLUTANTS IN BIOGAS

The main pollutants in biogas are water vapor (moisture), hydrogen sulphide and ammonia, which have a corrosive effect [8].

5.1. Pollutants Removal and Treatment Methods

5.1.2. Washing with Water Method

Biogas washed with water which provides purification for both hydrogen sulfur and carbon dioxide. Biogas is poured into the water column bottom and then accumulates on the top [28].

5.1.3. Pressure Spread Adsorption Method

By using activated carbon, methane and carbon dioxide are separated from each and other gasses in a pressurized environment [29].

5.1.4. Membrane Method

Membranes process is applied as both high-pressure gas separation and gas-liquid adsorption. High-pressure gas membranes can be used to combine hydrogen sulfide and carbon dioxide in the column at %96 purity. Gas-liquid adsorption, on the other hand, creates an interface between microporous hydrophobic membranes and gases and liquids while dissolves both hydrogen sulfur and carbon dioxide from each other [28].

6. SOME TYPES OF REACTORS FOR BIOGAS PRODUCTION

In anaerobic treatment, many types of reactors can be used according to the conditions and the raw material [30]. The main reactors were listed below:

1. Batch Reactor
2. Fully Stirred Reactor

3. Airless Contact Reactor
4. Piston Flow Reactor
5. Anaerobic Filter Reactor
6. Up-flow Anaerobic Sludge Bed Reactor
7. Film Reactors
8. Two-Stage Airless Treatment Systems

7. BIOGAS PRODUCTION FACILITIES

Biogas diversity increases due to waste types, environmental conditions, usage of raw material and other similar factors. Therefore, it is classified as follows [14,23,35]:

1. Agricultural biogas facilities
2. Wastewater treatment plants
3. Solid waste treatment plants
4. Industrial biogas plants
5. Landfill gas recovery facilities

8. ADVANTAGES AND DISADVANTAGES OF BIOGAS PLANTS

- The waste that will perish in nature is prevented from polluting the environment, and heat and electricity are generated as energy generation.
- It reduces the greenhouse gases released into the atmosphere, complies with the Kyoto Protocol, and is decreased from the disgusting in the storage areas. Disposal areas are reduced by cheap recycling technology.
- Efficient fertilizer is provided.
- Compared to other anaerobic processes, maximum organic loading rates and minimum sludge occur during reactions.

- Reactions take place in healthier and hygienic conditions
- The problem of unemployment decreases by workers and experts increase in the business sector.
- Biogas is both flammable and explosive.
- Diseases occur due to pathogenic bacteria
- Water consumption may increase depending on the type of waste
- The fertilizer yield may decrease depending on the type of raw material.
- Initial investment costs may be high depending on some regions and the type of raw material [31-34].

9. ENERGY SOURCES AND BIOGAS STATE OF WORLD AND TURKEY

Turkey's energy demand is increasing from 1970 to now. Turkey primary energy supply is shown in Figure 7 [35].

Turkey begins to consume natural gas like oil and coal as energy sources and also important needs which tabulated in Table 5. In Turkey that the natural gas was compared with other energy sources in Table 6. Because of energy requirement, biogas plants will be established in the future instead of natural gas and will be the main energy source in Turkey [36].

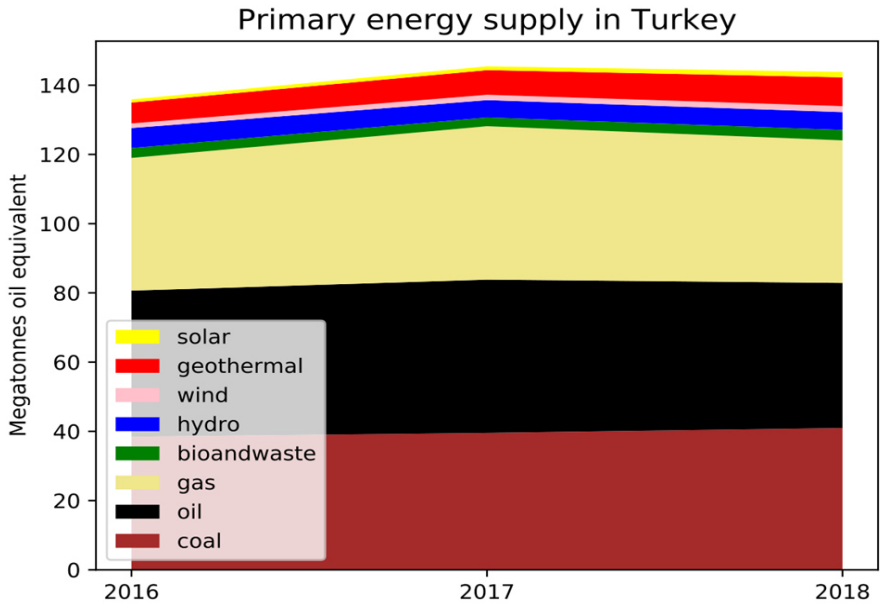


Figure 7. The Energy of Turkey [36]

Table 5. Total Import and Export of Energy source of [36]

Energy Source (TWh/y)	Import	Export
Coal	159.7	0
Lignite	0	0
Petroleum	425.3	84.3
Wood	0	0
Natural Gas	405	6.9

Table 6. Turkey Energy Source Production/Consumption Probability [36]

Energy Source (TWh/y)	Energy Production (MJ/y)			Energy Consumption (MJ/y)		
	2010	2015	2020	2010	2015	2020
Bituminous Coal	213.2	199.1	199.1	723.6	112.5	2016.2
Lignite	753.7	1012.8	1341.6	753.5	1012.8	1341.2
Asphaltite	12.6	12.6	12.6	12.6	12.6	12.6
Petroleum	65.8	44.8	29	1724	2111	2550.5
Natural Gas	9.8	8.9	9.6	1557	1873.5	2157.7

Table 7, waste sludge consisting of various organic compounds is at the highest level in both biogas yield and methane ratio production.

Table 7. Different types of waste and biogas efficiency [37]

Raw Material Waste	Total Solid (TS) (%)	Volatile Solid (TS) (%)	Biogas Efficiency (L/kg.VS)
Cattle	5-25	75-85	200-350
Chicken (Egg)	10-35	70-75	310-620
Chicken (Meat)	50-90	60-80	550-650
Sheep/Goat	30	20	90-310
Horse	25-30	60	200-350
Pork	3-16	70-80	250-550
Wheat Straw	70-90	85-93	200-300
Corn	80	91	350-480
Rice	89	93	170-280
Grass	20-25	89-90	280-550
Bagasse	65	78	140-190
Vegetable	5-20	75-86	300-400
Human	20-27	75	310-400
Leaf	80	90	300-400
Milk Process	8-12	90	350-800
Concentrate Milk Process	20-25	90	800-950
Fruit	15-20	75	250-500
Food	10-18	80-95	500-600

It is estimated that the total biogas plants which established in the world after 2012, are more than 10,000. % 80 of the biogas plants

have small scale energy as 500 kW or less. In the future, 100 facility projects of 500 kW and over are planned to approach. According to the 2013 International Energy Agency report, 1.5% of the electricity in the world in 2010 is produced from biomass wastes. Turkey has made studied from 1980 to produce biogas. Due to this, the "Law on the Use of Renewable Energy Resources for Electricity Generation" has been enacted [38,39].

In 2015 at EU, 654 PJ of biogas was equivalent to 18 billion m³ methane gas as a primary energy source. This amount is equal to half of the world's biogas production [40]. In 2016, there are more than 17,400 small and large biogas plants have been founded in the EU [41].

Although, Turkey has an important source of biogas potential which the resource not yet used at the desired level. While the installed electricity capacity in our country is 40 thousand MW but, the amount of electricity produced from biogas is only 15 MW. Turkey has a great potential for biogas as animal waste and agricultural wastes. It is estimated that it can reach the capacity of over 2,000 biogas plants that can operate in the world [42]. However, in Turkey 1,000 biogas plants is aimed to construct in 2019 and will be available. Most of the working biomass plants are as municipal or industrial wastes. There are many small facilities in the agricultural sector. But the number of operating facilities cannot be determined [43].

The Biogas Plant has been taken into operation and in 2018, a total of 8 facilities were put into operation in Turkey and total numbers of

biogas plants come out 28. Installed power and actual electricity generation of these biogas plants were given in Table 8 [44-47].

Table 8. Turkey biogas plants and 2017 electric energy production [46,47]

Plant Name	Established Power		Electrical Energy Production (kWh)	Net Electrical Energy Production (kWh)
	(MWm)	(MWe)		
Afyon Biogas Power Plant	4,125	4,017	28.119.000,00	26.655.634,00
Afyon-1 Biogas Power Plant	8,68	8,4	58.800.000,00	4.800.306,40
Ahi Suluova Biogas Tesisleri	1,3	1,067	46.459.000,00	0,00
Akıncı Energy Sandıklı Biogas Plant	1,4	1,4	9.800.000,00	3.954.868,30
Aksaray OSB Biogas Plant	6,57	6,402	44.814.000,00	34.183.690,00
Aksaray Yapılcan Biogas Power Plant	1,234	1,2	8.400.000,00	0,00
Albe-I Biogas Power Plant	3,11	3,017	21.119.000,00	7.222.242,80
ARF Ödemiş Biogas Plant	0,621	0,6	34.076.000,00	0,00
As Koç Biogas Plant	1,095	1,067	29.876.000,00	0,00
Atlas Construction Burdur Biogas Plant	1,556	1,506	21.084.000,00	0,00
Beypazarı Biogas Plant	0,827	0,793	16.665.600,00	27.760,00
Ceylanpınar Biomass Power Plant	0,466	0,45	18.676.000,00	0,00
De Solar 7 Biogas Power Plant	3,285	3,201	22.407.000,00	0,00
Edincik Biogas Power Plant	2,19	2,126	14.938.000,00	4.693.860,00
Gönen Biogas Plant	3,717	3,621	25.347.000,00	9.510.980,00
Karacabey 2 Biogas Plant	6,57	6,402	44.814.000,00	31.427.940,00
Karaman Biogas Plant	1,5	1,414	9.898.000,00	10.239.979,69
Kumrular Biogas Power Plant	4,38	4,268	29.876.000,00	377.511,60
Oğuzeli Biogas Power Plant	1,1	0,998	6.986.000,00	0,00
Ovacık Biogas Power Plant	4,96	4,8	33.600.000,00	3.488.025,00
Pamukova Biogas Plant	1,446	1,4	9.670.000,00	2.001.020,00
Polatlı Biogas Power Plant	1,551	1,471	10.297.000,00	7.665.705,10
Senkron Efeler Biogas Power Plant	3,72	3,6	33.600.000,00	18.557.352,45
Sezer Bio Energy Biogas Plnt. Biomass Pr.	0,624	0,5	3.500.000,00	1.304.945,00
Sigma Suluova Biogas Plant	1,02	1	14.000.000,00	415.711,00
Tire Biogas Power Plant	1,24	1,2	33.600.000,00	0,00
Tire Biogas Plant	4,96	4,8	29.876.000,00	17.254.520,00
Yapılcanlar2 Biogas Power Plant	1,095	1,067	7.469.000,00	229,27

10. CONCLUSION

All over the world and Turkey energy production and consumption increase in a parallel way as population growth and technological developments by reducing of petroleum fuels while the increase of surrounding problems in contrast of demand of new alternative energy resources.

Thus, agriculture, animal and other waste are crucial sources for the income of Turkey and other countries. One outcome product is biogas, renewable energy source, is a significant fuel with high calorific value. The biogas is a mixture of methane and carbon dioxide predominantly formed by the decomposition of organic parts of waste as a result of anaerobic.

Wastes and animal manure, industrial wastes, vegetable, fruit and food wastes, municipal organic wastes and wastewater treatment plant wastes are now considered raw materials for biogas production. Finally, Turkey has an available alternative, clean energy source from waste to biogas production.

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CHAPTER 4
SEMICONDUCTORS AND P-N JOINT SOLAR CELL

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1. INTRODUCTION

Although the semiconductor device field is a relatively new field of study, it has a tremendous impact on our society and the global economy. This is because semiconductor devices serve as the foundation of the world's largest industry. The devices until the production of the first study on metal-semiconductor contact in 1874 were very small. Entering the modern electronics era, the invention of the bipolar transistor in 1947 and the most important device for integrating the MOSFET in 1960, its circuits, was the invention of semiconductor memory in 1967, and most recently the technology driver of the electronics industry since 1990. It is thought that we have an extensive literature on semiconductor device physics and technology. There are more than 300,000 articles published in this field.

Semiconductor technology has also led to advances in solar cells. Solar cells are useful for both space and terrestrial applications. Solar cells provide power supply to satellites for a long time. The solar cell is an important candidate for an alternative energy source. Because solar cells can convert sunlight directly to electricity with good efficiency, they can provide permanent power at low cost and are not harmful to the environment. Radioactive energy emanating from the sun is provided by a nuclear fusion. As a result of the fusion reaction, approximately 6×10^{11} kg of hydrogen is converted into helium with a net mass loss of 4×10^3 kg per second. According to the Einstein relation ($E = mc^2$), this mass difference corresponds to an energy of

4×10^{20} J. This energy is emitted from ultraviolet to infrared (0.2 to $0.3 \mu\text{m}$) as electromagnetic radiation. The total mass of the sun is about 2×10^{30} kg and it can emit energy as radioactive energy for 10 billion years. The solar constant is defined as the intensity of solar radiation in space at the average distance between the sun and the earth and is 1353 W/m^2 . The grading of sunlight reaching the earth by interacting with the atmosphere is defined by air mass. Figure 1 shows two curves for solar spectral radiation (unit wavelength and power in the field). The upper curve representing the solar spectrum outside the earth's atmosphere satisfies the air mass zero condition (AM0). AM0 spectrum concerns satellite and spacecraft applications. On the other hand, the air mass one spectrum (AM1) represents the sunlight reaching the earth with a power of 925 W/m^2 when the sun is directly on top. The differences between the AM0 and AM1 spectra arise due to the atmospheric attenuation of sunlight. This difference is mostly caused by the absorption of ultraviolet rays in the ozone layer, the absorption of infrared rays by water vapor and scattering with dust in the air [1-10].

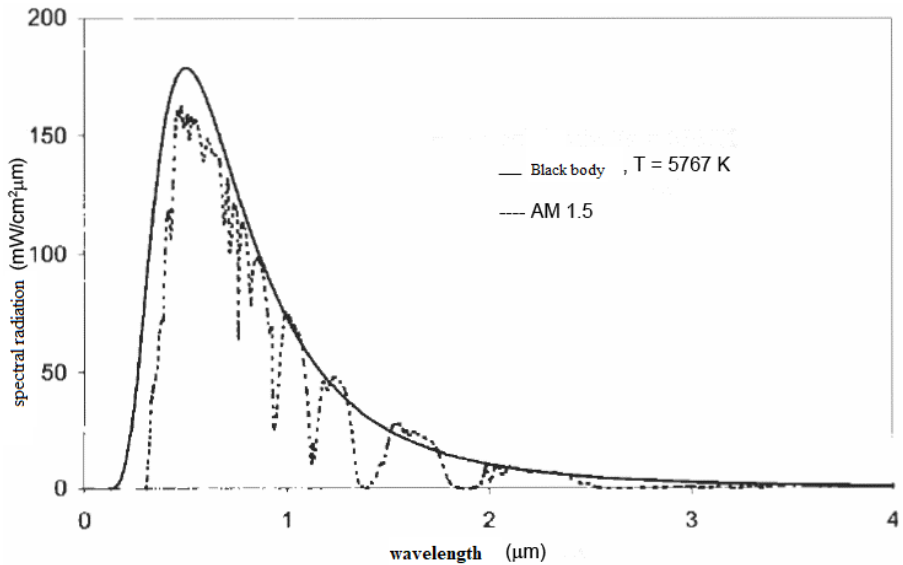


Figure 1 Solar spectral radiation [10]

2. SEMICONDUCTORS

Solid-state materials can be divided into three groups as insulators, semiconductors and conductors. While insulators such as quartz and glass have very low conductivities between 10^{-18} and 10^{-8} S/cm, conductors such as aluminum and silver have high conductivities between 10^4 and 10^6 S/cm. Semiconductors are materials with conductivity values between insulators and conductors. The conductivity of semiconductors is generally sensitive to temperature, light, magnetic field and the number of foreign atoms in their structure. This property in the conductivity of semiconductors has made them an important material in electronic applications. Table 1 shows some elements and compound semiconductors [11].

Table 1 Some elements and compound semiconductors [11]

Element	IV-IV Compounds	III-V Compounds	II-VI Compounds	IV-VI Compounds
Si	SiC	AlAs	CdS	PbS
Ge		AlSb	CdSe	PbTe
		BN	CdTe	
		GaAs	ZnS	
		GaP	ZnSe	
		GaSb	ZnTe	
		InAs		
		InP		
		InSb		

2.1. ENERGY BANDS

An isolated atom can only have certain energy values. For example, the energy levels of the hydrogen atom according to the Bohr model can be given as:

$$E_n = \frac{-13,6}{n^2} eV \quad (2.1)$$

Here, n is the lead quantum number. Energy values are -13.6 eV for the base level ($n=1$) and -3.4 eV for the first stimulated level ($n=2$). When we consider the same two atoms, the atoms have the same energy levels while they are separate from each other. When atoms approach each other, the same energy levels will be split into two energy levels due to the interaction between them. When N atoms come together to form a crystal, it will be divided into N energy levels which are very close to each other. This will cause the formation of a continuous energy band.

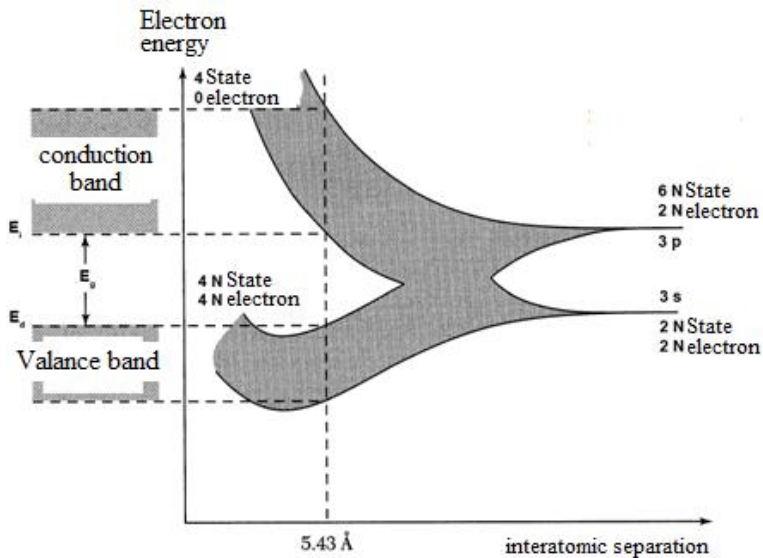


Figure 2.1 Schematic representation of the formation of a diamond lattice crystal from insulated silicon atoms.

Figure 2.1 shows a schematic representation of the formation of a diamond lattice crystal from isolated silicon atoms. Each atom has certain energy levels (two energy levels are seen on the far right of the figure). When the distance between atoms decreases, each degenerate energy level splits to form a band. When the distances between atoms are further reduced, energy levels fuse to form a single band. When the distance between atoms reaches the balance between the atoms of the diamond mesh (5.43 Angstroms for silicon), this band is divided into two bands again. These bands are separated from each other by a range of energy that electrons cannot pass. This energy range is called the forbidden bandgap and is denoted by E_g . The upper band of these bands is called the conductivity band and the lower band is called the valence band. Energy band diagrams of insulators, semiconductors and conductors are given in Figure 2.2.

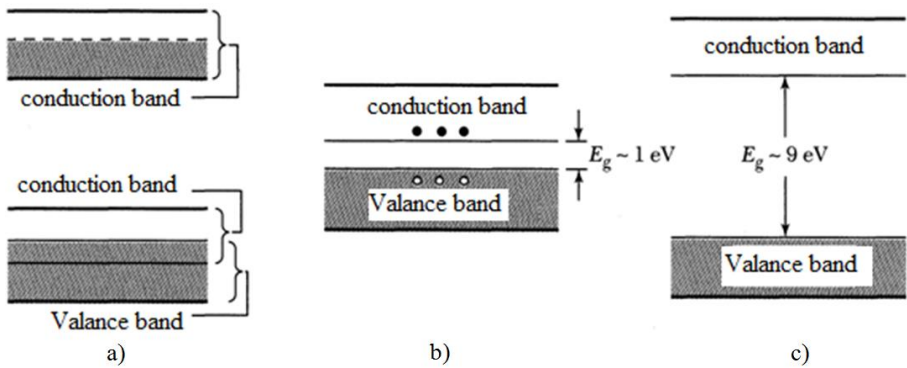


Figure 2.2 Energy band diagrams of insulators, semiconductors and conductors.[11]

In an insulator such as SiO_2 , valence electrons are tightly bound with neighboring atoms. These bonds are very difficult to break and so there are no free electrons to contribute to current conduction. As can be seen from the energy band diagram given in Figure 2.2a, there is a wide bandgap. While the valence bands of the insulators are filled with electrons, the conductivity bands are empty. Electrons cannot pass from the valence band to the conductivity band by applying thermal energy or an external electric field. In this context, SiO_2 is an insulator and cannot conduct electricity. In semiconductors, the bonds between atoms are relatively strong. Therefore, thermal vibration can break some bonds. When a bond breaks, a free gap is formed with a free electron. As shown in Figure 2.2b, the bandgap of the semiconductor is not as wide as the bandgap of the insulator (for example, the bandgap for silicon is 1.12 eV). Therefore, some electrons can pass from the valence band to the conductivity band by leaving gaps behind. When an electric field is applied, electrons and gaps gain kinetic energy and provide the conduction of electricity.

In conductors, the valence band and the conductivity band overlap with each other. Therefore, conductors have no band gap and easily conduct electricity under an electric field. As previously defined, the region between the lowest energy level of the conductivity band and the highest energy level of the valence band is called the forbidden energy bandgap. E_C represents the lowest part of the conductivity band and E_D represents the top of the valence band. E_C is the potential energy of the electron. The kinetic energy of the electron is measured above E_C . Similarly, E_D is the potential energy of the gaps. The kinetic energies of the gaps are measured in the part below the E_D value.

2.2. Pure carrier density

In pure semiconductors, electrons are excited from the valence band to the conductivity band as a result of thermal vibration and leave an equal amount of gap in the valence band.

The electron density in the conductivity band can be given by the following equation:

$$n = N_C \exp\left[-\frac{E_C - E_F}{kT}\right] \quad (2.2)$$

Here, E_C is the energy level of the conductivity band, E_F is the Fermi level, k is the Boltzman constant, T is the temperature and N_C the active state density in the conductivity band. N_C can be given by the following equation:

$$N_C = 2 \left[\frac{2\pi m_n kT}{h^2} \right]^{3/2} \quad (2.3)$$

Here, m_n is the effective mass of electrons and h is the Planck constant. The void density in the valence band is given by Equation 2.4.

$$p = N_V \exp\left[-\frac{E_F - E_V}{kT}\right] \quad (2.4)$$

Here, E_V is the energy level of the valence band; N_V is the active state density in the valence band. N_V can be given by Equation 2.5:

$$N_V = 2 \left[\frac{2\pi m_p kT}{h^2} \right]^{3/2} \quad (2.5)$$

Here, m_p is the effective mass of holes. In pure semiconductors, the following equation can be written, where n is the density of electrons, p is the density of holes and n_i is the density of pure carrier.

$$n = p = n_i \quad (2.6)$$

The Fermi level of pure semiconductors can be given with the help of Equation 2.2 and Equation 2.4.

$$\begin{aligned} E_F = E_i &= \frac{E_C + E_V}{2} + \frac{kT}{2} \ln \left[\frac{N_V}{N_C} \right] \\ &= \frac{E_C + E_V}{2} + \frac{3kT}{4} \ln \left[\frac{m_p}{m_n} \right] \end{aligned} \quad (2.7)$$

Here, E_i is the Fermi level of the pure semiconductor and is very close to the middle of the forbidden bandgap at room temperature. For pure semiconductors;

$$np = n_i^2 \quad (2.8)$$

and,

$$np = N_C N_V \exp\left[-\frac{E_g}{kT}\right] \quad (2.9)$$

Here, E_g is the forbidden band gap and can be given as;

$$E_g = (E_C - E_V) \quad (2.10)$$

2.3. Acceptor and Donor

When a semiconductor is doped with foreign atoms, the semiconductor becomes doped and impurity energy levels are formed. Figure 2.3 shows the replacement of a silicon atom with Arsenic and Boron atoms.

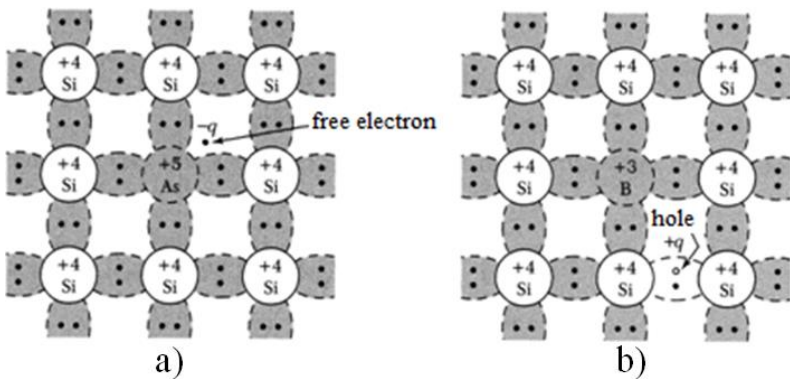


Figure 2.3 The replacement of a silicon atom with Arsenic and Boron atoms [11]

Figure 2.3.a shows the replacement of a silicon atom with an arsenic atom. Figure 2.3.a shows the replacement of a silicon atom with an arsenic atom. The pentavalent arsenic atom forms a covalent bond by sharing its four electrons with four neighboring silicon atoms. The

fifth electron remains free and crosses the conductivity band to become the conduction electron. The silicon semiconductor doped with an arsenic atom becomes n-type semiconductor. In this case, the Arsenic atom is called the donor (acceptor). On the other hand, when the silicon semiconductor is doped with trivalent boron atom, as seen in Figure 2.3.b, the boron atom takes an electron from the silicon atom to form the fourth covalent bond and causes a gap to form. In this case, as the boron atom receives electrons, Boron-doped silicon semiconductor is also called a p-type semiconductor [11].

The donor atoms generally have the energy to be fully ionized at the room temperature. This situation is called complete ionization. In the case of complete ionization; the electron density can be given by Equation 2.11;

$$n = N_D \quad (2.11)$$

Here, N_D is the transmitter density.

The Fermi level can be written in terms of active state density N_C and donor concentration N_D in the conductivity band.

$$E_C - E_F = kT \ln \left[\frac{N_C}{N_D} \right] \quad (2.12)$$

Similarly, gap concentration can be written.

$$p = N_A \quad (2.13)$$

Where N_A is the concentration of receptors. For this case, the Fermi level can be given as:

$$E_F - E_C = kT \ln \left[\frac{N_V}{N_A} \right] \quad (2.14)$$

As can be understood from Equation 2.12, if the high transmitter concentration and the E_C - E_F energy difference are small, the Fermi level will be close to the conductivity band. Similarly, high acceptor concentration will shift the Fermi level towards the valence band.

It is more useful to write the electron and gap concentration of the doped semiconductors with n_i which is the carrier density of the pure semiconductor, and E_I which is the Fermi level of the pure semiconductor.

$$n = n_i \exp \left[\frac{E_F - E_I}{kT} \right] \quad (2.15)$$

And,

$$p = n_i \exp \left[\frac{E_I - E_F}{kT} \right] \quad (2.16)$$

2.4. Drift current

2.4.1. Mobility

Electrons in a semiconductor have three degrees of freedom and can move in three-dimensional space. Therefore, the kinetic energy of electrons in a state of thermal equilibrium can be written as:

$$\frac{1}{2} m_n v_{th}^2 = \frac{3}{2} kT \quad (2.17)$$

Where m_n is the effective mass of the electron, v_{th} is the average thermal velocity.

The distance between two collisions is called the average free path. The time elapsed between two collisions is called the average free time and is denoted by τ_c . Under an ε electric field, electrons gain velocity under the $-q\varepsilon$ force. This velocity is called drift velocity and is denoted by v_n . The net thermal velocity is zero due to random collisions. So there is only a net drift velocity under an electric field. In this context, the drift velocity can be written as below:

$$v_n = - \left[\frac{q\tau_c}{m_n} \right] \varepsilon \quad (2.18)$$

$$\mu_n = \frac{q\tau_c}{m_n} \quad (2.19)$$

Where μ_n is called the mobility of the electron. In this case, the drift velocity of electrons is expressed by Equation 2.20.

$$v_n = -\mu_n \varepsilon \quad (2.20)$$

Similarly, drift velocity for holes is expressed in Equation 2.21.

$$v_p = -\mu_p \varepsilon \quad (2.21)$$

Where μ_p is the mobility of holes.

2.4.2. Resistivity

As stated earlier in this study, electrons are exposed to the $-q\varepsilon$ force under an electric field. This force is equal to the negative gradient of

the potential energy of the electron. Therefore, the electric field can be expressed by Equation 2.22.

$$\varepsilon = \frac{1}{q} \frac{dE_i}{dx} \quad (2.22)$$

E_c energy level, which is the lowest part of the conductivity band of an electron, represents the potential energy of that electron. Here, E_i is used instead of E_c as the potential energy because E_i will be used instead of E_c in the formation of p-n joints.

$$\varepsilon = -\frac{d\psi}{dx} \quad (2.23)$$

With the help of Equations 2.22 and 2.23, the equation establishing a connection between electrostatic potential and potential energy is obtained.

$$\psi = -\frac{E_i}{q} \quad (2.24)$$

The transport of the carriers under the effect of an electric field generates the drift current. Consider a semiconductor with cross-section A , length L and carrier density n , as shown in Figure 2.4.

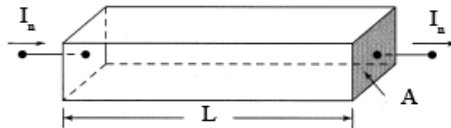


Figure 2.4 Semiconductor with cross-section A , length L and carrier density n

When an electric field is applied to this semiconductor, the electron current density J_n passing through the sample can be written as:

$$J_n = \frac{I_n}{A} = \sum_{i=0}^n (-qv_i) = -qnv_n = qn\mu_n \varepsilon \quad (2.25)$$

where I_n is the electron current. Similarly, the current density for gaps can be expressed by the following equation:

$$J_p = qnv_p = qn\mu_p \varepsilon \quad (2.26)$$

The total drift current density of the semiconductor under the electric field is as follows;

$$J = J_n + J_p = (qn\mu_n + qn\mu_p) \varepsilon \quad (2.27)$$

$$\sigma = qn\mu_n + qn\mu_p \quad (2.28)$$

It is called the conductivity coefficient. If the resistivity of a semiconductor can be written in terms of ρ conductivity by Equation

$$\rho = \frac{1}{\sigma} = \frac{1}{q(n\mu_n + p\mu_p)} \quad (2.29)$$

Usually, only one of the components in equation 2.26 or 2.27 is used in pure semiconductors due to the large difference between the two carriers. Therefore, the resistivity in equation 2.28 can be expressed as equation 2.29 for n-type semiconductor and equation 2.30 for p-type semiconductor.

$$\rho = \frac{1}{qn\mu_n} \quad (2.30)$$

$$\rho = \frac{1}{qn\mu_p} \quad (2.31)$$

2.4.3. Diffusion flow

Drift current occurs when an external electric field is applied to semiconductors. Another important current is the diffusion current that occurs due to the difference in carrier density in the semiconductor. Electron transfer takes place towards the region with lesser density than the region with high carrier density. In this case, the diffusion current can be given by the following equation,

$$J_n = -qF = qD_n \frac{dn}{dx} \quad (2.32)$$

and the direction of current is opposite to the direction of electron flow. Where,

$$D_n = v_{th}l \quad (2.33)$$

And, that is known as the diffusion coefficient. On the other hand, q is the charge of electron, F net carrier flows, l average free path, and dn/dx carrier density concerning the position. Equation 2.32 can be written more usefully using the energy co-division theorem for the one-dimensional case.

$$\frac{1}{2} m_n v_{th}^2 = \frac{1}{2} kT \quad (2.34)$$

If equations 2.19 and 2.34 are written in their places in equation 2.32 and $l = v_{th}\tau_c$ relation is used, the following Equation 2.35 can be obtained.

$$J_n = qD_n \frac{dn}{dx} = q \left[\frac{kT}{q} \mu_n \right] \frac{dn}{dx} \quad (2.35)$$

Thus, the *Einstein equation* is obtained.

$$D_n = \left[\frac{kT}{q} \right] \mu_n \quad (2.36)$$

This relation is related to the diffusion coefficient and mobility, two important constants that characterize the carrier conduction resulting from diffusion and drift in a semiconductor. Similarly, the Einstein relation can be written in gaps.

2.4.4. Current density equations

When an external electric field with the difference in concentration is applied, a drift current will occur in addition to the diffusion current. In this case, the total current density for electrons at any location will be the sum of drift and diffusion current.

$$J_n = q\mu_n n \varepsilon + qD_n \frac{dn}{dx} \quad (2.37)$$

Similarly, the total current density of the gaps can be calculated.

$$J_p = q\mu_p p \varepsilon - qD_p \frac{dp}{dx} \quad (2.38)$$

The minus sign is used here, as the gaps will move in the $-x$ -direction for a positive gap gradient. This creates diffusion current in the $-x$ -direction. The total conduction current density can be expressed as:

$$J_{cond} = J_n + J_p \quad (2.39)$$

2.5. P-N Joint

When two semiconductors of the p-type and n-type are in contact with each other, the p-n junction is formed. The most important feature of the p-n junction is that it passes current in only one direction. In the case of correct supply, the current increases exponentially with increasing voltage. In the case of reverse supply, current does not flow. When the voltage is increased in the opposite direction, the current increases suddenly after a certain point. This situation where the current suddenly increases is called the breakpoint. A p-n joint plays an important role in modern electronics applications. It is mostly used as rectifier and switch in electronic circuits. In Figure 2.4, energy band diagrams are given before two p-type and n-type semiconductors come together and when they come together.

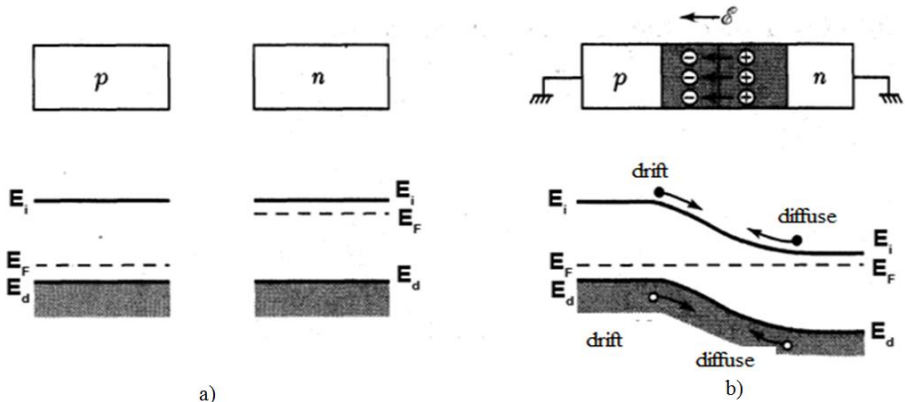


Figure 2.4 Energy band diagrams before two p-type and n-type semiconductors come together and when they come together [11]

In Figure 2.4.a, energy band diagrams are given before two p-type and n-type semiconductors come together. While the Fermi level is close to the valence band in p-type semiconductors, it is close to the conductivity band in n-type semiconductors. The p-type

semiconductor has a high vacuum density, and the n-type semiconductor has a high electron density. When these two semiconductors come together, the p-n junction is formed. Due to the high carrier density difference in contact, gaps diffuse from the p-type region to the n-type region, and electrons diffuse from the n-type region to the p-type region. While the gaps leave the p side, some negatively charged acceptor ions near the junction form a negative charge region. Similarly, while electrons leave the n-type region, some positively charged donor ions also form a positive charge region. When equilibrium is reached, an electric field is generated from the n-type region to the p-type region. This electric field is in the opposite direction of the diffusion currents. When a steady state is reached; the net current at the junction will be zero. Thus, the drift current caused by the electric field must reset the diffusion current due to the density difference. In Figure 2.4.b, the contact form of the p-n junction is given. Equation 2.40 can be written by the help of Equation 2.38, Equation 2.22 and Equation 2.36.

$$\begin{aligned}
 J_p &= J_p(\text{drift}) + J_p(\text{diffuse}) \\
 &= q\mu_p p \varepsilon - qD_p \frac{dp}{dx} \\
 &= q\mu_p p \left[\frac{1}{q} \frac{dE_i}{dx} \right] - kT\mu_p \frac{dp}{dx} = 0
 \end{aligned} \tag{2.40}$$

The gap density can be given by Equation 2.41.

$$p = n_i e^{(E_i - E_F)/kT} \tag{2.41}$$

Equation 2.42 can be obtained by deriving the density of the gap.

$$\frac{dp}{dx} = \frac{p}{kT} \left[\frac{dE_i}{dx} - \frac{dE_F}{dx} \right] \quad (2.42)$$

By equation 2.41, the net void current density can be expressed by Equation 2.43 or Equation 2.44.

$$J_p = \mu_p p \frac{dE_F}{dx} = 0 \quad (2.43)$$

or

$$\frac{dE_F}{dx} = 0 \quad (2.44)$$

Similarly, the electron current density can be written in Equation 2.45.

$$J_n = \mu_n n \frac{dE_F}{dx} = 0 \quad (2.45)$$

From this, it can be understood that the Fermi level must be constant along the x-axis for the net value of electron and gap currents to be zero. The electrostatic potential ψ_p in the p-type region can be expressed by Equation 2.46.

$$\psi_p = -\frac{kT}{q} \ln \frac{N_A}{n_i} \quad (2.46)$$

The electrostatic potential ψ_n in the n-type region can be expressed by Equation 2.47.

$$\psi_n = \frac{kT}{q} \ln \frac{N_D}{n_i} \quad (2.47)$$

The total electrostatic potential difference between the p-type and n-type regions in thermal equilibrium is shown as V_{bi} and is called the built-in potential.

$$V_{bi} = \psi_n - \psi_p = \frac{kT}{q} \ln \frac{N_A N_D}{n_i^2} \quad (2.48)$$

2.6. Radiant transitions and optical absorption

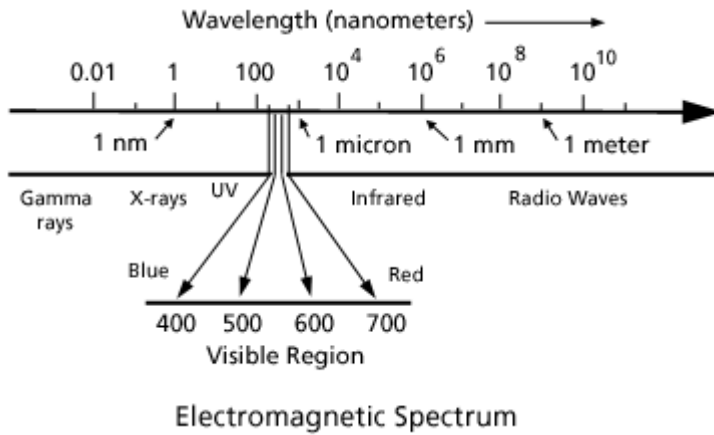


Figure 2.5 Electromagnetic spectrum of the optical region [11]

Figure 2.5 shows the electromagnetic spectrum of the optical region. The light that the human eye can perceive only falls between $0.4\mu\text{m}$ and $0.7\mu\text{m}$. The ultraviolet zone is between $0.01\mu\text{m}$ and $0.4\mu\text{m}$. The infrared range is between $0.7\mu\text{m}$ and $1000\mu\text{m}$. The following equation is used to convert wavelengths to photon energy.

$$\lambda = \frac{c}{\nu} = \frac{hc}{h\nu} = \frac{1.24}{h\nu(\text{eV})} \mu\text{m} \quad (2.49)$$

Where, c denotes the speed of light in vacuum, ν the light frequency, h Planck's constant, $h\nu$ the photon energy.

2.6.1. Radiant transitions

There can be three types of interactions between a photon and an electron in a solid: absorption, self-propagation, and excitation propagation. Consider the two energy levels of an atom as E_1 and E_2 . Let, E_1 represent the ground state and E_2 the excited state. Any transition between these two levels causes a photon of frequency ν_{12} to be emitted or absorbed due to the energy difference $h\nu_{12} = E_2 - E_1$. Most of the atoms are fundamental at the room temperature. This situation is broken when a photon with $h\nu_{12}$ energy enters the system. When an atom in the E_1 state absorbs the photon, it rises to the E_2 level. Figure 2.6 shows the change in energy level as a result of photon absorption.

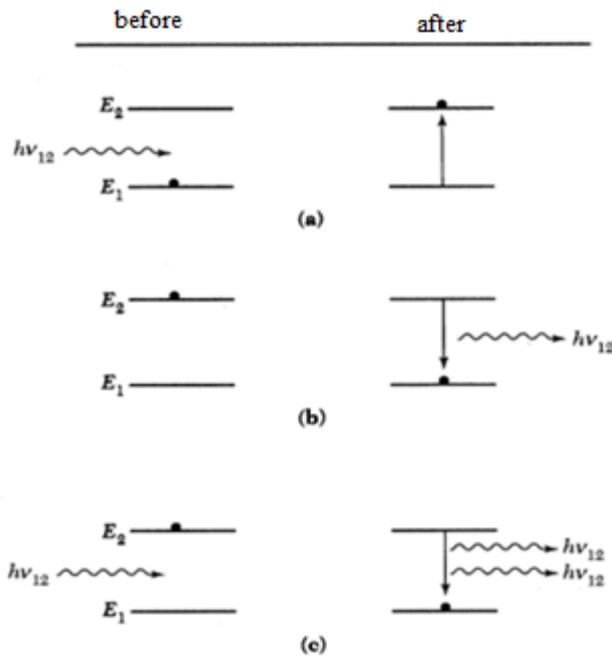


Figure 2.6 Absorption between Photon and Electron [11]

When Figure 2.6 is examined, the excited state of the atom is not stable and within a short time without any intervention, it spontaneously releases a photon of $h\nu_{12}$ energy and becomes the base state. This situation is called self-propagation (oscillation) and is also seen in Figure 2.6.b. When a photon of $h\nu_{12}$ energy enters the system while the atom is in an excited state, the atom can pass to the base level by emitting a photon with the energy of $h\nu_{12}$ and in phase with the incoming photon. This is called excitation propagation (Figure 2.6.c). The radiation resulting from excitation propagation is monochromatic because each emitted photon has the same $h\nu_{12}$ energy and phase. Light-emitting diodes (LEDs) do the self-emitting process, lasers do the propagation process by excitation, photodetectors and solar cells are based on the absorption process.

2.6.2. Optical absorption

There are usually several optical absorption processes, each contributing to the total absorption coefficient (α). This mechanism consists of (i) primary absorption process (ii) exciton absorption (iii) absorption due to additives and defects (iv) absorption due to intermediate band transitions and (v) free carrier absorption. When the photon energy is greater than the energy range, the absorption process results from the passage of electrons from the full valence band states to the empty conductivity band states. In cases with less energy than the energy range, the absorption mechanism is caused by excitons and transitions between impurities and band states. Free carrier absorption

due to the transitions within the energy bands causes a continuous absorption at low energies.

In the basic absorption process, a photon excites an electron from the valence band to the conductivity band. In this process, both energy and momentum must be conserved. While the photon momentum is small concerning the crystal momentum, the absorption process must maintain electron momentum. When the minimum of the conductivity band and the maximum of the valence band have the same wave vector k , the direct transition occurs and the material becomes a direct-band semiconductor. If the band ends do not have the same wave vector, the transitions are indirect and the material becomes an indirect-band structure semiconductor. In such semiconductors, an extra particle such as a phonon must be added to the system for the momentum conservation. However, such a process is less likely to occur than with direct passes. Therefore, the baseline absorption is generally less in indirect-band semiconductors than in direct-band semiconductors.

Optical absorption is determined by an absorption coefficient α , that can be derived from transmission measurements. Transmission $T=I/I_0$ can be written as follows where I_0 is the intensity of the incident light, I is the intensity of the passing light and R is the reflection;

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1-R^2 \exp(-2\alpha d)} \quad (2.50)$$

In the above equation, d is the thickness of the material. For large values of αd , Equation 2.50 can be expressed by Equation 2.51.

$$T = (1 - R)^2 \exp(-\alpha d) \quad (2.51)$$

Equation 2.52 can be obtained by reducing Equation 2.51.

$$I = I_0 \exp(-\alpha d) \quad (2.52)$$

In Figure 2.7, the transition between bands is shown.

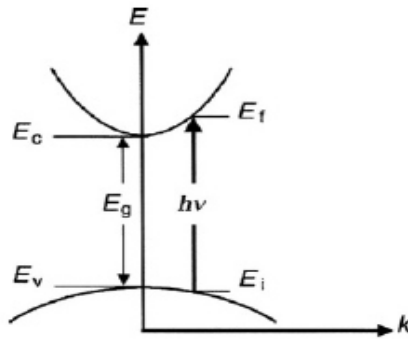


Figure 2.7 Transition between bands [11]

The absorption coefficient can be derived from the following simple operation with the direct transitions between parabolic bands in Figure 2.7. The P_{if} transition probability, n_i and n_f , respectively, are the electron density in the initial state and the empty energy levels in the final state, the absorption coefficient can be expressed as:

$$\alpha(h\nu) = A \sum P_{if} n_i n_f \quad (2.53)$$

For electron energy;

$$E_e = \frac{\hbar^2 k^2}{2m_e^*} \quad (2.54)$$

and, for gap energy;

$$E_h = \frac{\hbar^2 k^2}{2m_h^*} \quad (2.55)$$

so, the transition energy, electron energy and vacuum energy, respectively

$$h\nu = \frac{\hbar^2 k^2}{2m_e^*} + \frac{\hbar^2 k^2}{2m_h^*} + E_g \quad (2.56)$$

$$h\nu - E_g = \frac{\hbar^2 k^2}{2m_e^*} + \frac{\hbar^2 k^2}{2m_h^*} = \frac{\hbar^2 k^2}{2m_r^*} \quad (2.57)$$

where $m_r^* = m_e^* m_h^* / (m_e^* + m_h^*)$ is the reduced effective mass. By the state density equation below:

$$N(h\nu)d(h\nu) = (2\pi^2 \hbar^3)^{-1} (2m_r^*)^{3/2} (h\nu - E_g)^{1/2} d(h\nu) \quad (2.58)$$

The absorption coefficient for direct transitions between parabolic valence and conductivity bands can be expressed as:

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2} \quad (2.59)$$

where, A is a constant of order 10^4 . The energy range E_g and $h\nu$ are in eV and α is cm^{-1} . Indirect band transition is shown in Figure 2.8.

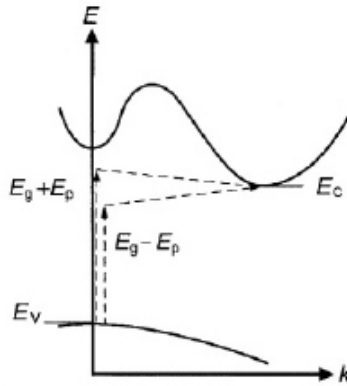


Figure 2.8 Indirect band transition [11]

When Figure 2.8 is examined, in indirect-band structured materials, the maximum energy of the valence band and the minimum energy of the conductivity band do not occur in the same wave vector k . In such a state, the transitions contain three particles of photons, electrons, and phonons to provide conservation of energy and momentum. Thus, in indirect transitions, momentum conservation is achieved by absorption or oscillation of a characteristic E_p valued phonon. The absorption coefficient in a transition involving phonon absorption can be given by the following equation.

$$\alpha_a(h\nu) = \frac{A(h\nu - E_g + E_p)^2}{\exp(E_p / k_B T) - 1} \quad (2.60)$$

3. P-N Joint Solar Cells

Figure 3.1 shows a schematic representation of the P-N joint solar cell.

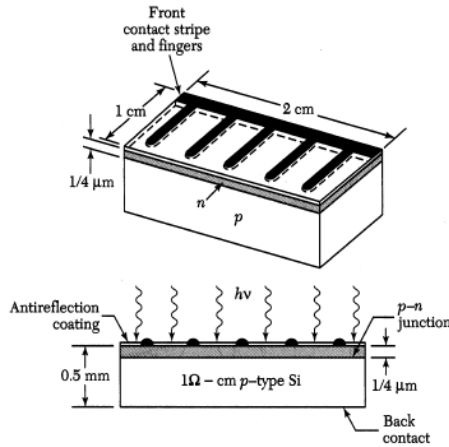


Figure 3.1 Schematic representation of the P-N joint solar cell

When the solar cell is exposed to the solar spectrum, a photon with energy less than the forbidden bandgap will not contribute to energy production. A photon with energy greater than the band E_g contributes to the output of the solar cell with an energy equal to E_g . Photon energy that exceeds the forbidden bandgap turns into heat. The energy band diagram of the P-N joint is given in Figure 3.2.

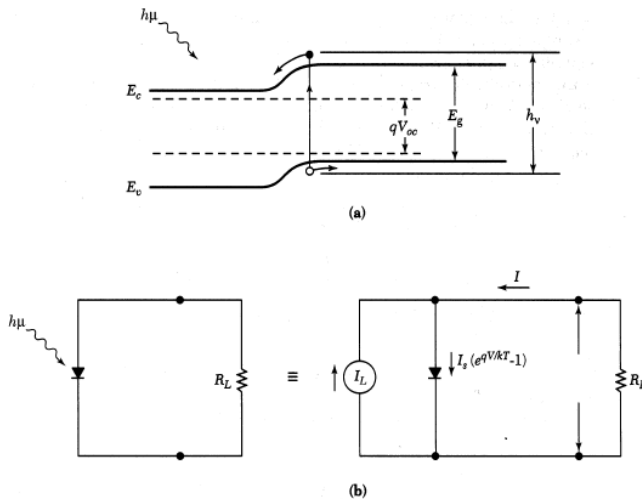


Figure 3.2. Energy band diagram of the P-N joint

In this context, we will consider the energy band diagram of an illuminated p-n joint in Figure 3.2.a to derive the transformation efficiency. The part of the solar cell circuit with a constant-current source parallel to the p-n joint is shown in Figure 3.2.b. The I_L source in the circuit is created by stimulating the carriers in the solar cell under the light. I_s diode saturation current and R_L is a resistance connected to the circuit. The ideal I-V characteristic of such a device is given by the following equation.

$$I = I_s(e^{qV/kT} - 1) - I_L \quad (3.1)$$

and,

$$J_s = \frac{I_s}{A} = qN_c N_v \left(\frac{1}{N_A} \sqrt{\frac{D_n}{\tau_n}} + \frac{1}{N_D} \sqrt{\frac{D_p}{\tau_p}} \right) e^{-E_g/kT} \quad (3.2)$$

where A is the surface area of the device. The I-V characteristics of the solar cell are given in Figure 3.3. The I-V characteristic of a solar cell from the above equation for $I_L=100$ mA, $I_s=1$ nA, $A=4$ cm² and $T=300$ K is shown in Figure 3.3.a.

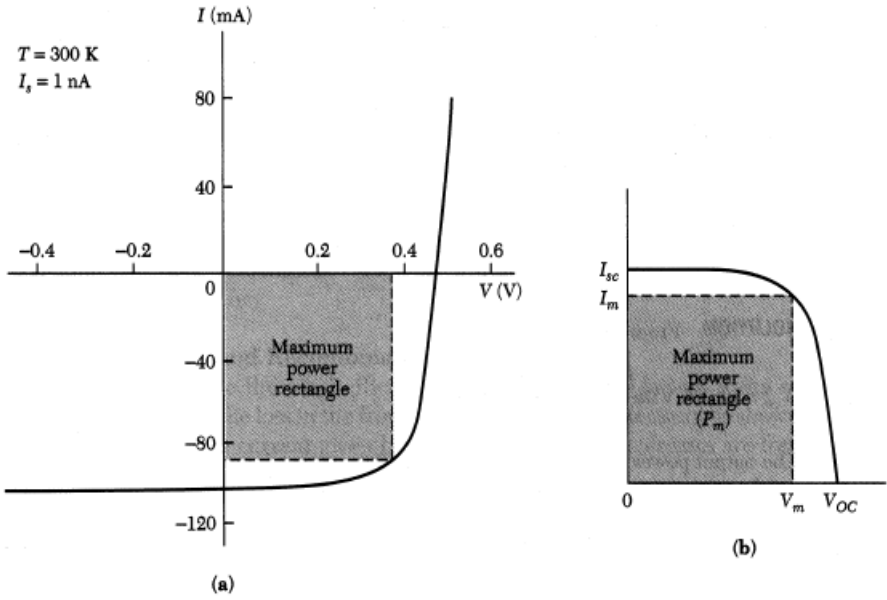


Figure 3.3. Solar cell's I-V characteristics [11]

In addition, another representation of the I-V characteristics of the solar cell is given in Figure 3.3. Where I_{sc} is the short circuit current of the solar cell equal to I_L and V_{oc} is the open-circuit voltage. The shaded region in the figure is defined as the maximum power rectangle. In the given Figure 3.3b I_m is the maximum current, V_m is the maximum voltage. The open-circuit voltage ($I = 0$) can be given by Equation 3.3.

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{I_L}{I_s} + 1\right) \cong \frac{kT}{q} \ln\left(\frac{I_L}{I_s}\right) \quad (3.3)$$

The output power can be expressed with Equation 3.4.

$$P = IV = I_s V \left(e^{qV/kT} - 1 \right) - I_L V \quad (3.4)$$

When $dP/dV=0$ condition is fulfilled, maximum power is obtained.

$$V_m = \frac{kT}{q} \ln \left[\frac{1 + (I_L / I_s)}{1 + (qV_m / kT)} \right] \cong V_{oc} - \frac{kT}{q} \ln \left(1 + \frac{qV_m}{kT} \right) \quad (3.5)$$

$$I_m = I_s \left(\frac{qV_m}{kT} \right) e^{qV_m / kT} \cong I_L \left(1 - \frac{1}{qV_m / kT} \right) \quad (3.6)$$

The maximum output power P_m , can be expressed in Equation 3.7.

$$P_m = I_m V_m \cong I_L \left[V_{oc} - \frac{kT}{q} \ln \left(1 + \frac{qV_m}{kT} \right) - \frac{kT}{q} \right] \quad (3.7)$$

The conversion efficiency of a solar cell is given by the following equation.

$$\eta = \frac{I_m V_m}{P_{in}} = \frac{I_L \left[V_{oc} - \frac{kT}{q} \ln \left(1 + \frac{qV_m}{kT} \right) - \frac{kT}{q} \right]}{P_{in}} \quad (3.8)$$

or,

$$\eta = \frac{FF \cdot I_L V_{oc}}{P_{in}} \quad (3.9)$$

In this efficiency equation, P_{in} is the power of the incident light and FF is the fill coefficient.

$$FF = \frac{I_m V_m}{I_L V_{oc}} = 1 - \frac{kT}{qV_{oc}} \ln \left(1 + \frac{qV_m}{kT} \right) - \frac{kT}{qV_{oc}} \quad (3.10)$$

4. CONCLUSION

In this study, properties and formation of semiconductors were examined. How the solar cell was formed with P and N-type semiconductor material was explained in detail. In this context, equations that can be used to study the current, voltage, power and efficiency of materials were derived. The use of these equations to determine and evaluate the electrical properties of a solar cell is thought to contribute to future studies.

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CHAPTER 5

**SCANNING ELECTRON MICROSCOPE AND ANALYSIS IN
SCANNING ELECTRON MICROSCOPE**

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1. INTRODUCTION

One of the methods of studying the properties or behavior of materials is optical inspection. These examinations were done with the naked eye or light microscope. However, it was not possible to see some detail or behavior. The most common obstacles that cause this are as follows;

- a) Insufficient separation power (resolution) and low magnification.
- b) Not obtaining detailed information about the chemical components of the material.
- c) Materials with rough surfaces are not examined at high magnifications.

For these reasons, it is possible to obtain detailed information from the microstructure, topography, morphology and chemical analysis of conductive materials with electron beam devices (electron microscopes). The most commonly used device in researches is the Scanning Electron Microscope (SEM). The pictures created under the microscope are created by counting the reflected electrons or the glows generated by the interaction of the electron beam with the material. These are secondary electron images, backscattered electrons, characteristic x rays, Auger electrons, etc. The reason for using SEM is that the sample to be examined is easy and practical to prepare. The samples with dimensions in centimeters (cm) can be analyzed with SEM.

H. Busch, who first studied particles in electric and magnetic fields with their charged orbits, showed in 1926 that these fields could behave like particles. Thus, he laid the foundations of the geometric electron in optics[1]. After this discovery, the idea of electron microscopy started to emerge and two teams were determined for test work in this area in Berlin. Of these work teams, one was Knoll and Ruska with Technische Hochschule and the other were collaborators in Briiche and its A. E. G. Laboratory. When the teams were successful, they attracted other employees to the field and thus a successful transmission electron microscope was built[2].

German scientists thought it was possible, in principle, to make a rather different electron microscope, known since then as a scanning microscope. The principle of such a device is schematically shown in Figure 1. From a cathode C, electrons are accelerated to high velocity and then pass through the lenses L1, L2 and L3. The current from B on an extremely thin probe passes through D1 coils to deflect the electron. Also, using D2 coils to deflect the beam, with such two sets of coils causing deflections at right angles to each other, the electron point on the focused sample and the point on the screen move the cathode ray tube in synchronization. Secondary and backscattered electrons accumulate in P and the obtained current passes from A to G. The G of the cathode ray tube and thus the picture formed on the tube face, in a sense, creates an image of the surface. Moreover, a highly magnified view can be made with the deflection coils by controlling the various currents [3]. Max Knoll produced the first SEM operating according to the above principles in 1935, and detailed

work continued with Knoll and Theile until 1939. Later, the first commercial SEM was produced [4]. Modern commercial SEM emerged from extensive development in the 1950s.

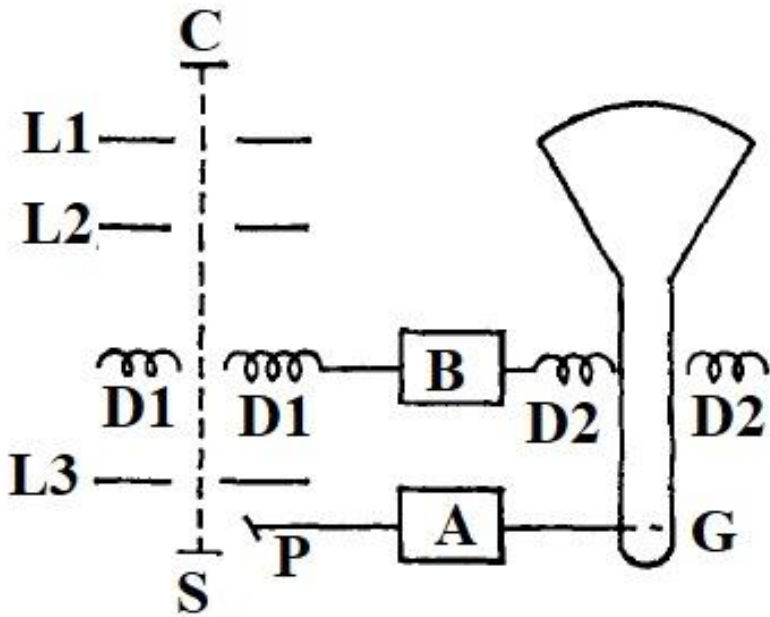


Figure 1. Principle of scanning electron microscope [3].

2. SCANNING ELECTRON MICROSCOPE

Scanning electron microscopy is a topographic examination method applied by scanning an electron beam across the sample of interest and detecting the scattered electrons from this sample and making an image [5]. Since it is possible to focus the electron beam in nm size, the resolution and detail provided by this method are very high. Scanning electron microscope generally consists of Electron source

(gun), Deflection coils, Magnetic Lenses, Aperture, Sample holder, Detectors and Vacuum chamber parts and is shown in Figure 2.1.

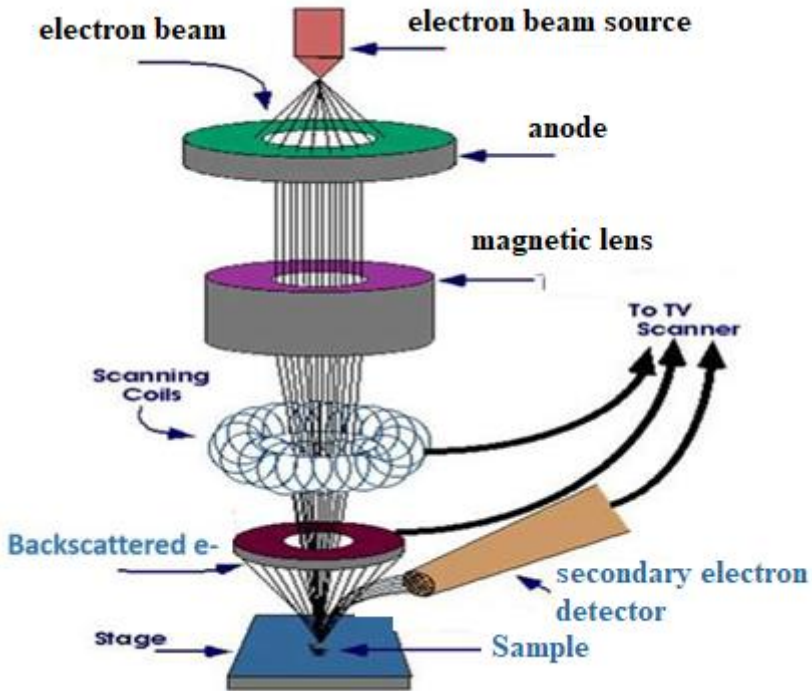


Figure 2.1. Schematic Representation of the Scanning Electron

2.1 Parts of the Scanning Electron Microscope

2.1.1. Electron Source (Gun)

Electron sources are the sources that generate enough electrons to concentrate on the sample. The filament is heated by applying an electric current. In this way, electrons with sufficient energy accumulate at the tip of the filament, forming an electron cloud. If a positively charged plate (Anode) is placed next to the filament, the electrons are under the influence of this anode. There are 3 types of electron guns.

- 1) Tungsten
- 2) Lanthanum hexaboride (LaB6)
- 3) Field emission electron guns

2.1.1.1. Tungsten Gun

In this weld, in order to make the diffusion surface very small, the 120 μm tungsten wire is twisted to form a thin tip. The filament heats up with the current passing through it and the filament heats up to 2700 $^{\circ}\text{C}$.

This gun has a life of 50-150 hours. It is cheap and needs 10^{-3} Pa operating vacuum. Tungsten gun is shown in Figure 2.2.

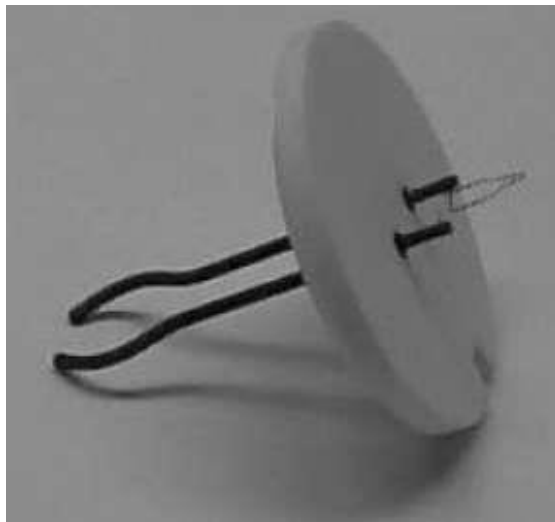


Figure2.2. Tungsten Gun

2.1.1.2. Lanthanum Hexaboride (LaB6) Gun

LaB6 electron gun is formed by placing the crystalline LaB6 on Tungsten or Rhenium. When voltage is applied, the crystal heats up and starts emitting electrons. It works at low temperatures. It is

durable enough to high currents. The LaB6 electron gun is shown in Figure 2.3.



Figure 2.3. Lanthanum Hexaboride (LaB6) Gun

2.1.1.3. Field Emission Electron Gun

Field emission electron Gun (FEG) has a tungsten-zirconium tip. It has the best resolving power and performance. Electrons are pulled from the wire under high vacuum and high magnetic field effect. There is no heating in this gun. Its solubility is 1/10 of the tungsten electrode and 1/5 of the LaB6. Its lifespan is 1000 times more than that of Tungsten filament. Field Emission Electron gun is shown in Figure 2.4.

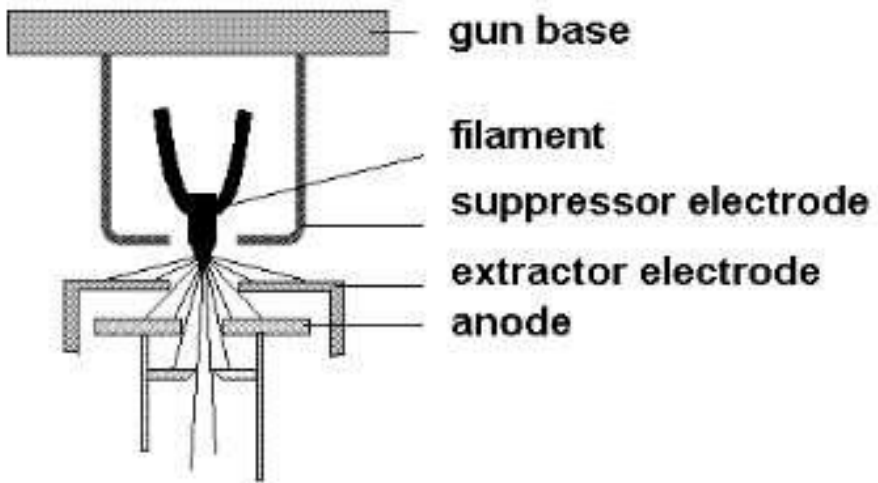


Figure 2.4 Field Emission Electron gun

Electron guns are compared in terms of their characteristics in Table 2.1.

Table 2.1. Features of electron guns

	Unit	W	LaB ₆	FEG
ϕ activation energy	eV	4.5	2.4	4.5
operating temperature	K	2700	1700	300
brightness	A/m ²	10 ⁹	5x10 ¹⁰	10 ¹³
energy scattering	eV	3	1.5	0.3
vacuum	Pa	10 ⁻²	10 ⁻⁴	10 ⁻⁸
lifetime	hour	100	500	>1000

2.1.2. Magnetic lenses and Deflection Coils

Magnetic lenses enable the electron beam generated from the electron gun to focus on the sample. The coils, on the other hand, allow the focused electron beam to be scanned throughout the sample.

2.1.3. Vacuum System

The vacuum system is very important in SEM and the pressure should be low enough not to interfere with the electron gun operation. Because it is desired to low to prevent the corrosion of the electron-emitting surfaces. Also, the vacuum is required for the electrons to interact with the molecules in the environment less. If there is no enough vacuum, dirt will accumulate on the surface. Such impurities will accumulate in the Electron Gun chamber and affect its performance. Because such surfaces reduce the sensitivity of voltage measurements. Electron gun chamber and column are taken to vacuum together.

2.1.4. Detector

The scanning electron microscope has more than one detector. There is a secondary electron detector, a backscattered electron detector. If desired, an X-ray detector, etc., can be added. The task of the detector is to collect the scattered electrons and radiations after the interaction of the electron beam with the sample and to create an image.

2.2. Electron-sample interaction

The electron beam obtained from the filament collides with the sample and the electrons spread in all directions. Some of the electrons are backscattered with almost no loss of energy, and the energy levels of the backscattered electrons (BSE) are around 30 keV. Secondary electrons are also emitted. The energies of these electrons are less than 50 eV. BSEs are collected by the solid-state detector. The intensity of

the beam going to the cathode ray tube can be adjusted by amplifying the signals from the detector with a multiplier. Thus, places with electron scattering on the monitor appear brighter than other areas. The energy of secondary electrons is much smaller than the energy of incoming electrons. X-rays are emitted in the sample. The resulting results fall into two categories;

1) Electron signals

1) Photon signals

The interactions between the incident electron beam and the samples are shown in Figure 2.5. Each of these interactions creates a separate image.

2.2.1. Image obtained from secondary electrons

These electrons occur due to the inelastic (leading to energy transfer) collision between the weakly bonded electrons or valence electrons in the conductivity band when the incoming electron beam interacts with the sample. The energy transferred is large enough to overcome the binding energies of electrons. Thus, the electron is removed from the sample under study. These electrons are called secondary electrons. Secondary electrons are low energy electrons. They can be easily collected by applying a positive voltage between 100-300V to the detector with a scintillation counter. In this way, 50-100% of secondary electrons can be collected. Thus, a 3-dimensional view of the studied area is obtained and shows the surface topography.

2.2.2. Image obtained from backscattered electrons

Backscattered electrons are formed due to elastic collisions between incident electrons and the nuclei of the atoms in the sample under study. The larger the atomic number of the atoms in the sample, much more backscattered electrons will be obtained. In an elastic collision, the energy loss of incident electrons is too small. Images obtained with backscattered electrons provide information about the atomic numbers of the atoms in the sample under examination. Elements with smaller atomic numbers reflect fewer than elastic electrons, and the larger the atomic number, the more elastically reflected electrons. This situation, which occurs due to the atomic number, creates a contrast in the SEM photograph. Shows surface topography and the effects of chemical dispersion on surfaces.

2.2.3. Image obtained from X-rays

When the high energy electron beam hits the surface of the sample, some electrons are detached from the sample surface due to the collision. If these electrons are detached from the inner orbitals, the atoms lose their stability. Since the energies of the electrons in the outer orbitals are higher than the energies of the electrons in the inner orbitals, the outer orbital electrons have to lose a certain amount of energy while filling the inner orbitals. This lost energy occurs in the form of X-rays. So, X-rays caused by the sample are detected by the detector. Electrons that cross the conductivity band are converted into electrical signals. Thus, the image is obtained. To perform X-ray analysis, a solid-state x-ray detector must be placed in the scanning

electron microscope. So this shows the chemical composition distributions. Interactions between the incident electron beam and the sample are shown in Figure 2.5.

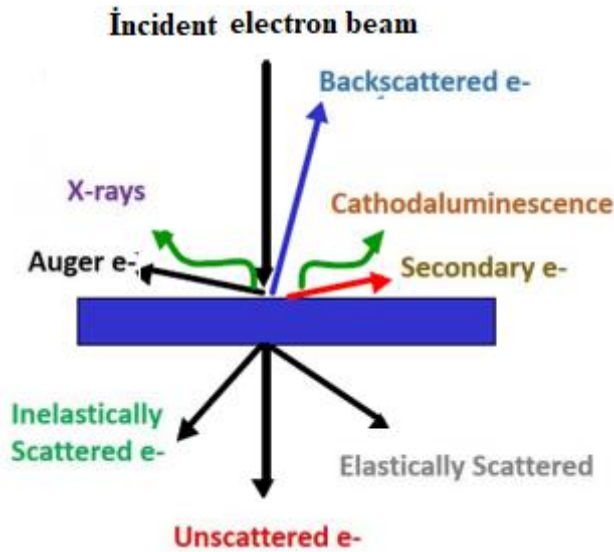


Figure 2.5. Interactions between the incident electron beam and the sample

2.2.4. Separating power

A modern light microscope has a maximum magnification of 1000x. The resolving power of the microscope is not only limited to the number and quality of the lenses, but also the wavelength of the light used for illumination. The reason for this is that the wavelength of the light used in the light microscope is between 400nm-700nm, ie the separation limit is around 200nm. The most important factor for this to happen is that the wavelength of the light used is approximately 550nm. In scanning electron microscopy, the separation force depends on the radius of the emitted electron beam (spot size). Electron is used instead of light in electron microscopes. Since the wavelength of the

electrons is approximately 100,000 times shorter than the wavelength of the light used in the light microscope, it allows the resolution and magnification of approximately 250,000 times magnification with additional lenses.

2.3. Working Principle of Scanning Electron Microscope

Electrons are emitted when the filament of the electron gun is heated up to a temperature of about 2800 °C in a vacuum. It is pushed from the filament with a negative potential of 30 keV. Electrons passing through the vacuum-evacuated column are focused on the sample with the help of magnetic lenses. Thus, the coil rings allow the focused electron beam to be scanned throughout the sample.

The scattering will occur when electrons interact with the sample so that the scattered electrons are collected in the corresponding detectors. The signal which coming from the detector is amplified by the multiplier and the intensity of the beam going to the cathode ray tube is adjusted. It is scanned synchronously with the incoming electron beam. Thus, when the focused electron beam is sent over the sample, the cathode rays on the tube, the regions of the sample emitting more electrons appear bright and other regions dark. Thus, the image is formed.

3. ANALYSIS OF THE SAMPLE

3.1. Sample Preparation for Analysis

Since the electron beam will be sent on the sample, the sample current occurs. If a detailed image or analysis is desired, it is necessary to absorb this current. Therefore, it is necessary to allow the excess electrons on the surface to flow to the ground in order to prevent charging. For analysis of insulating materials, it must be coated with a conductive material. For this purpose, the sample placed on a metal platform is coated with a metal such as gold, palladium, gold-palladium and carbon-gold.

3.2. Analysis Results

The 1000-fold and 20,000-fold magnified images of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin-film taken in the ZEISS brand Scanning electron microscope are given in Figure 3.1 and Figure 3.2.

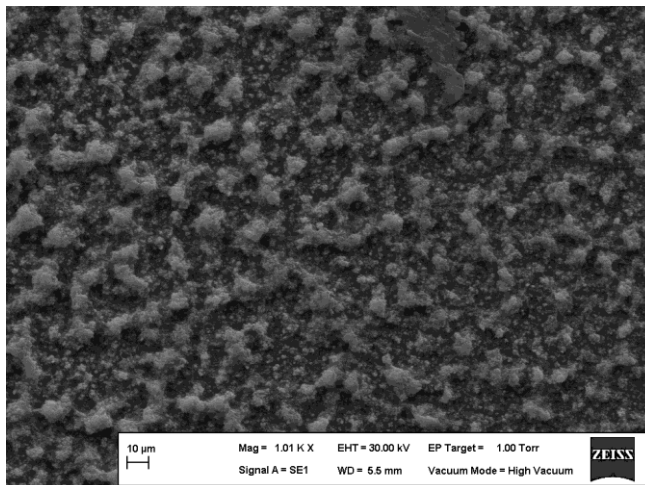


Figure 3.1 Morphological view of CZTS at 1000 times magnification

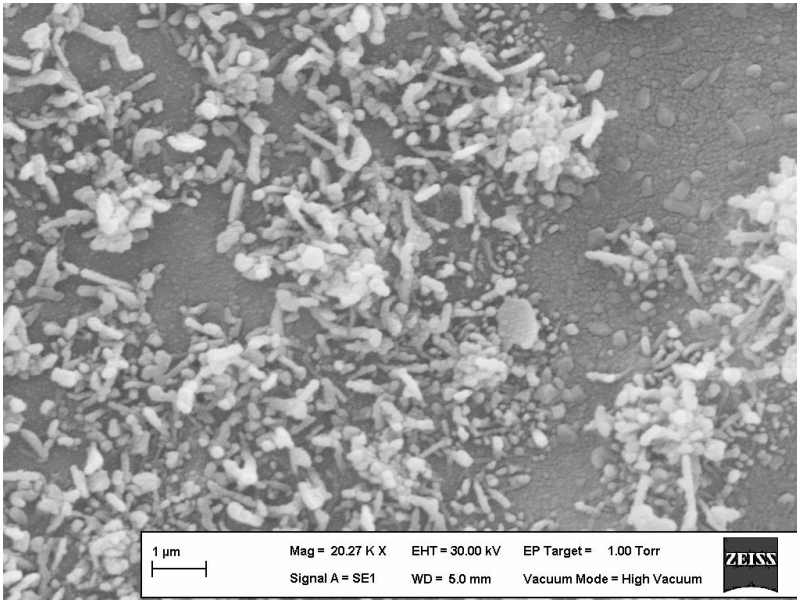


Figure 3.2 Morphological view of CZTS at 20,000 times magnification

4. CONCLUSION

Scanning electron microscope device (SEM) is more useful for examining rough surface and small-sized samples, due to its high resolution and high depth of field. Scanning Electron microscope also gives images showing the microstructure of materials at high magnifications. If an X-ray detector is used in the scanning electron microscope, the distribution and chemical analysis of the elements in the studied sample can also be done. In this context, the use of scanning electron microscope will provide both convenience and more accurate results in academic studies.

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CHAPTER 6

**BEHAVIOUR, DESIGN AND STRENGTHENING
TECHNIQUES OF MASONRY STRUCTURES AGAINST
EARTHQUAKE EFFECTS**

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1. INTRODUCTION

When masonry structures are mentioned, starting from the meaning of the word "pile up" or "overlap", it is possible to understand the structures constructed in this way more easily. Masonry structures, which are essentially a construction system, refer to the structures built by stacking or overlapping, which we have defined for a long time. In other words, the construction systems in which the load is carried by the walls are called 'Masonry Structures'. Of course, it is seen that Hasol who defines masonry structures in two groups as Masonry and Wooden masonry structures in the Architecture Dictionary. For masonry, stones or bricks are stacked as a carrier with a binding mortar. For the wooden masonry structure, he defined that it as massive structures made by overlapping with wood and logs.

In this study, Masonry Structures are examined as a building type. Masonry structure built in Turkey where is being built with masonry material shows that a large proportion of so-called masonry buildings. It can be seen as the reason why masonry structures are widespread in other regions outside the Black Sea region, as they are advantageous in terms of ease of material supply, economical and easy construction due to local resources. It is also known as a name that includes materials such as masonry and stone brick. Therefore, masonry structures are produced by knitting natural and/or building materials such as stone, brick, briquette, sandstone with or without mortar. Walls in masonry structures, living room, room, kitchen, bathroom,

WC etc. While performing an architectural function that separates the spaces from each other, they also undertake the role of bearing.

Despite these construction and preference advantages, generally it isn't qualified as earthquake resistant structures because they are very heavy. It's constructed with brittle materials such as stone bricks, and it has little resistance to dynamic and horizontal loads such as earthquakes. So in this study; Turkey, especially in masonry recently experienced an earthquake of this intensity has been shown in several instances that they create the overall effects on masonry structures. In these examples, there are masonry buildings that are not engineered, especially in rural areas, and the damage of these buildings has been pointed out. In particular, strengthening techniques that can be applied to both these damaged buildings and the earthquake-resistant design of undamaged or newly constructed masonry buildings are presented. Strengthening techniques stated in terms of applicability are the results of studies conducted in various universities, and it is known that these strengthening techniques are supported by laboratory experimental results.

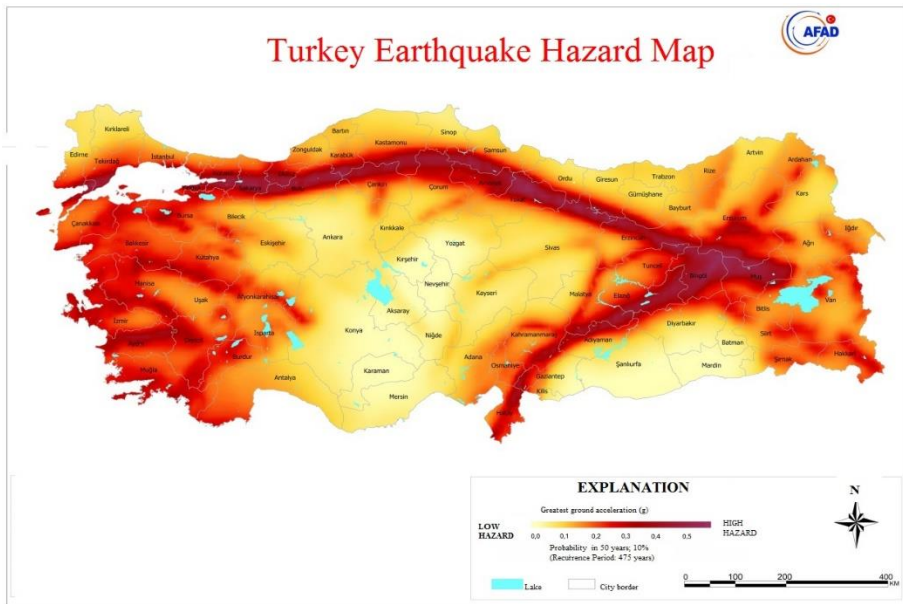
In Turkey, the observations made in the construction and operating reserves, in the countryside of the city is determined that the right production system encountered serious volatility. Especially in city centers, the density of reinforced concrete carcass, steel and prefabricated structures is observed, while in rural areas this density is composed of wooden structures in the Black Sea region and masonry structures in other regions. It is observed that masonry structures with

a high density of illegal buildings are seen to be a significant density in city centers, especially in places that are low socio-economically, even suburban areas. We see that most of these structures were built using completely local materials, using traditional techniques, many of them either by poorly crafted masters or by the cooperation of individuals, so their spouses and relatives, without any engineering service. In this case, even when considered together with the fact that Turkey is a country of earthquakes, especially it shows us clearly the reasons for the grave consequences that occur in rural areas. We live in an earthquake in Turkey and the earthquake in countries like Japan experienced violence taken into consideration in comparison with the earthquake, how our damages and casualties We remember that great every time. Although the dire results, we encountered as a result of earthquakes such as the 1999 Marmara and 2011 Van earthquakes have increased the number of scientific studies on earthquake-resistant masonry design and strengthening of these structures, we can say that the implementation of these studies is still not sufficient.

2. TURKEY'S ROLE IN THE EARTHQUAKE ZONE

Turkey, located in the Alpine-Himalayan seismic belt and 95% of the population lives in the earthquake zone (SIS). The majority of the studies for earthquake-resistant construction in our country are carried out on reinforced concrete carcass and steel construction systems due to the building stock and the tendency to build multi-story buildings. On the other hand, it cannot be said that studies have been carried out on wooden and masonry structures with the same approach.

Earthquakes occurring in our country, together with reinforced concrete carcass-framed building and steel structures built in cities, cause more damage to masonry structures built especially in rural areas. Map 1 given below from AFAD 's prepared by 2019 in Turkey is an earthquake hazard maps and Schedule 1, the total population, total area, considering the total building number and carrier systems are disclosed affect the rate of earthquakes. Looking at these rates; The amount of masonry structures, at least as well as reinforced concrete carcass and steel structures, shows that intensive work must be done to obtain designs with sufficient earthquake safety.



Map 1. Turkey Earthquake Hazard Map (AFAD-National Earthquake Research Program)

Table 1. According to earthquake zones; the number of buildings and load-bearing structure system distribution (SIS)

Earthquake Zones	Total Number of Buildings	Earthquake Zones	Total Number of Buildings
I. Degree Earthquake Zone	2.142. 402	1183 623	939 695
II. Degree Earthquake Zone	2.131.028	1113 141	1004825
III. Degree Earthquake Zone	1.265. 111	608 026	651 920
IV. Degree Earthquake Zone	1.686. 137	712 206	964 689
No-Danger Zone	484 458	94 337	388 206

Masonry structures are generally emerging as intense in rural areas in Turkey. Since such structures are built without sufficient engineering knowledge and arbitrarily, they are damaged or destroyed in earthquakes and cause loss of life and property.

For example, in an earthquake of 6.3 magnitudes in Erzincan on 13 March 1992, a total of 8000 buildings, 6120 of which are single-story, 1700 of which are double-story and 180 of which are three-story unreinforced masonry structures, were either severely damaged or also collapsed (Ural, A.)

Also, on Sunday, October 23, 2011, a devastating 7.2 magnitude earthquake occurred in the village of Tabanlı, Van province. In this earthquake, masonry buildings, which constitute the majority of the buildings, were damaged greatly. According to the AFAD 2011 Van Earthquake report, 89 out of every 100 buildings in the villages of Van Center were severely damaged. It is known that the building

systems in the villages are masonry. Both Erzincan and Van these data on earthquakes, both in May 2003 Bingöl earthquake belonging to Figure 1 and Figure 2, Van earthquake belonging to Figure 3 and Figure 4, in Turkey shows the results emerging after the earthquake in masonry buildings.



Figure1. Bingöl Earthquake (Karaşin, A.H., Karaesmen, E.)



Figure2. Bingöl Earthquake (Karaşin, A.H., Karaesmen, E.)



Figure3. From Van Earthquake



Figure4. From Van Earthquake

The perception that most of the buildings damaged by the earthquakes we experienced are multi-storey and reinforced concrete carcass structures. It can be said that the reason for this is that the number of casualties in these buildings is high and collective. However, it is

accepted by everyone that reinforced concrete carcass buildings serve as engineering and that these structures are produced in an earthquake-resistant manner, that is, as long as the horizontal loads caused by the earthquake are taken into account, these structures will be resistant to existing earthquakes. From here, we can say that the damage rates of reinforced concrete carcass structures are not very high, but those that are not built by the legislation, in other words, defective or even defective structures are destroyed. Especially in the countryside and so on, it is seen that the masonry structures built do not receive engineering services and therefore the damage rates are too high. We can see this from the results of the Erzincan earthquake given above. As can be seen from the figures, even in masonry buildings, we see that the number of damage increases as the number of floors decreases. The amount of damage has always been high in single-story houses, which people call "a house where we can tread our heads" and which can be called almost free of cost, with low costs in terms of cost.

The earthquake is caused by the vibration of the earth's crust, forcing the structure to move from its supports and creates a dynamic effect on the structure. The structure must be designed and built resistant to this effect. The main principle of durable building design is not to damage the system elements in mild earthquakes, to repair structural and non-structural damages in moderate earthquakes, and to prevent the partial and complete collapse of the structure in severe earthquakes (Gürdil, F.A.)

3. MATERIALS USED IN MASONRY BUILDINGS

When selecting the materials used in the construction of masonry structures, these structures may differ depending on factors such as the region where these structures are built, production conditions, consumer needs and production technologies. In Turkey, especially in recent times and usually natural stone masonry structure built today on the foundation, walls again, natural stone, artificial stone blocks, sandstone, brick, or adobe was built using bricks and so on. However, reinforced concrete and wooden floors, soil, wood, concrete roofs or roofs were formed as other elements of the structure. Generally, it is possible to classify the materials as follows;

- Threshing Brick
- Factory Brick
- Natural stone
- Adobe Blocks
- Concrete Briquette
- Light Concrete Blocks
- Binders etc. materials are used in the construction of masonry walls.

4. MASONRY CONSTRUCTION BEHAVIOR

Since the materials such as stone, brick and briquette used in the construction of masonry structures are heavy, the masonry structures are also heavy. This situation causes the occurrence of great inertia

forces during an earthquake, and therefore large internal stresses occur in the walls.

Horizontal forces that come to masonry structures during an earthquake are carried by the walls. Under the horizontal forces on the walls, the wall section acts like a beam resting on the roof, floor slab or ground, and transfers the load on it to the adjacent floors or roof (Figure 5). These floors, which are called diaphragms, transmit the horizontal load to the sidewalls on which they sit in such a way that there is an in-plane force. Under these loads, side walls operate as horizontal and vertical load-bearing masonry walls (Figure 6). This is the case if there is a connection between the roof and the wall that will ensure the transfer of force. (Çöğürçü, M.T.)

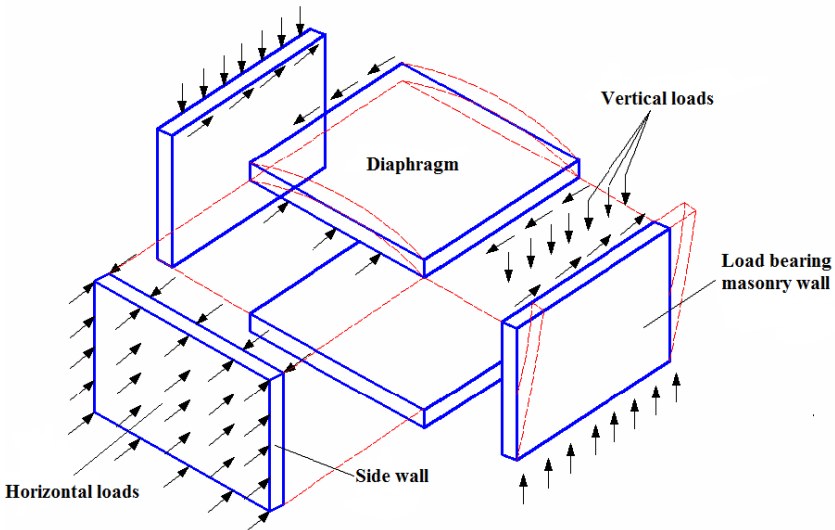


Figure 5. Distribution of horizontal load on walls (Çöğürçü, M.T.)

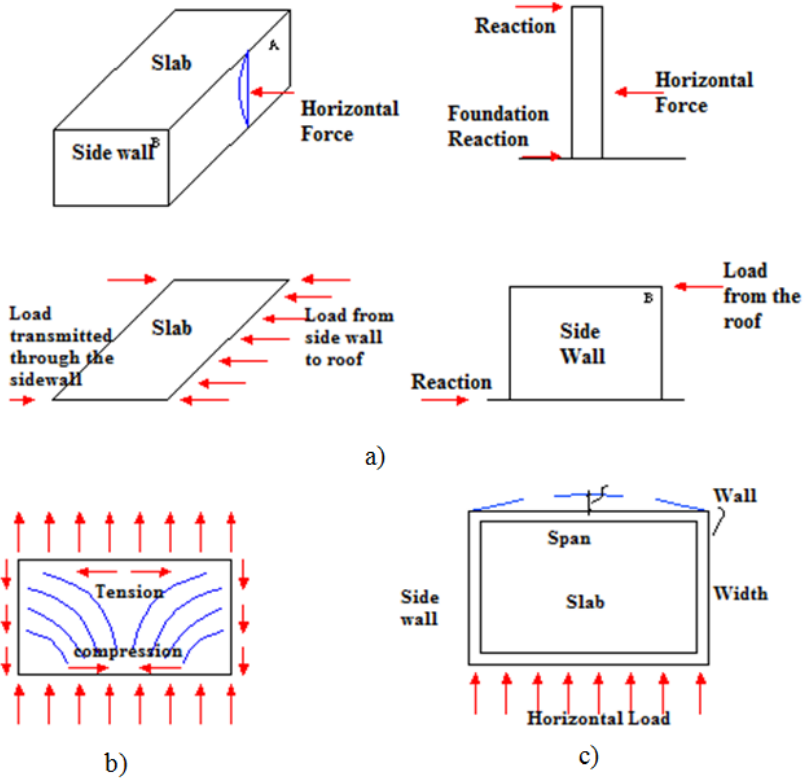


Figure 6. Distribution of earthquake load overbearing elements in masonry structures (Bayülke, N.)

- a) Distribution of horizontal loads in masonry structures b) Stress distribution in floors c) Deformation on floors and walls under horizontal loads

The masonry walls are also affected by axial forces coming from the floor and roof slab (Kaya, E). These loads create shear forces on the wall parallel to the plane of the wall. For the loads from the upper parts of the building to be transmitted to the load-bearing walls on the lower floor, the floor slabs must be rigid enough against the horizontal load. In this case, the forces are distributed over the walls in proportion to their rigidity. In the case of deformation of the floors,

the vertical load on the building is not proportional to the rigidity of the walls (Bozdoğangil, A.T.)

During the transfer of the earthquake load from the roof to the ground, shear stresses occur in the wall. If the shear strength of the wall is exceeded, 45 degrees bent tensile cracks occur in the solid wall. The angle of these cracks changes according to the size of the axial pressure in the wall. If there are large vertical compressive stresses, this angle will be greater than 45 degrees. Since the earthquake is a two-way motion, oblique tensile cracks occur in the other direction. After the oblique tensile cracks weaken the wall once, the wall becomes unable to bear the vertical loads it previously could carry. During an earthquake, there is an increase or decrease of 20-30% in vertical loads. This is a feature of the dynamic loading that continues during the earthquake. Thus, vertical pressure cracks also occur after oblique tensile cracks. As the structures are forced in both principal directions at the same time with the horizontal forces, the stress accumulation occurs especially at the corners of the structures, as can be seen in Figure 7. To prevent this type of damage, reinforced concrete columns can be placed at the corners of the structures or the corners can be rounded. Damages may occur if the masonry walls are not connected with reinforced concrete floors or roof floors or if they are connected with flooring that is not rigid enough (Çöğürçü, M.T.)

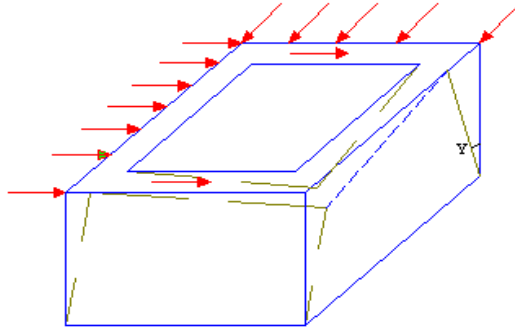


Figure 7. Building corners under horizontal forces (Çöğürçü, M.T.)

When both horizontal and vertical load-bearing masonry walls become unable to carry these loads, three different collapses occur on the walls as shown in Figure 8.

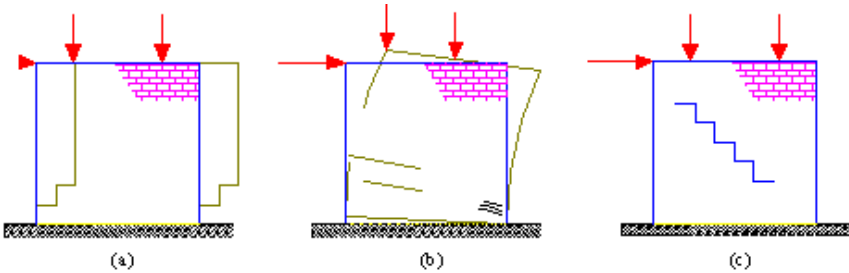


Figure 8. Collapse patterns in horizontal and vertical load-bearing walls (Çöğürçü, M.T.)

a) Horizontal translation collapse b) Bending collapse c) Shear failure

5. EARTHQUAKE RESISTANT DESIGN

Studies on the performance of earthquake-resistant building design and reinforcement methods in our country have focused on reinforced concrete, steel and partially wooden structures. Since masonry structures are made of non-continuous materials, their real behavior cannot be expressed mathematically. The strength of the brick wall, which is a composite material, cannot be expressed in terms of the

strength of the brick and mortar components. The formulas developed on this subject and based on certain acceptances could not be verified with the experimental results (Bayülke, N.)

Masonry structures are constructed from heavy, bulky and brittle materials. The inertia forces that will occur during the earthquake are directly proportional to the weight of the structure. In other words, the heavier the structure, the more inertia forces occur during an earthquake. This means that the building elements will be subjected to enormous internal effects. Structural elements made of brittle material suddenly collapse without deformation during an earthquake. (Çöğürçü, M.T.)

The dimensioning and equipping of masonry structures are carried out according to the rules in ‘ABYYHY’ (Regulation on buildings to be built in disaster areas) along with the current standards and regulations or the ‘DBYBHY’ (Regulation on Buildings to be Built in Earthquake Zones) updated in 2007.

In terms of earthquake-resistant building design, undesired symmetrical plan types are shown in Figure 9.a, symmetrical and undesired plan types are shown in Figure 9.b, and the types of plans that are broken into the desired shape are shown in Figure 9.c (Kalkan, N.)

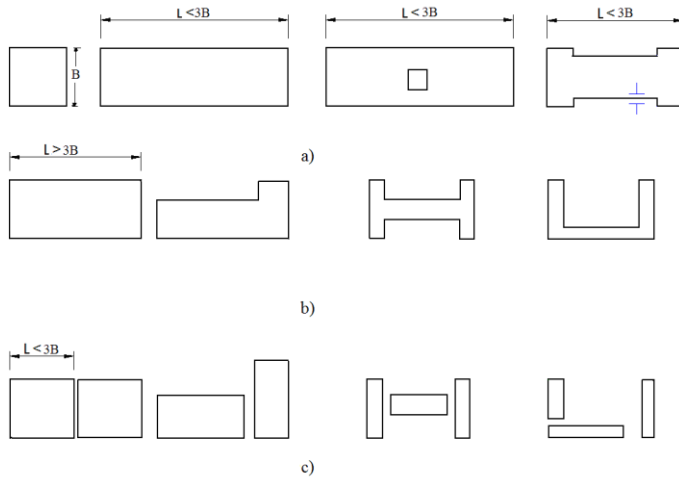


Figure 9. Suggested plans for earthquake resistant buildings (Kalkan, N)
a) Symmetrical plan types b) Symmetrical and undesired plan types c) fragmented block structures

6. EARTHQUAKE STRENGTHENING METHODS OF MASONRY STRUCTURES

Mainly the purpose of strengthening masonry structures; We can say that we have been living for many years and we have been suffering and saddened by the nation, and we can say that all actions to be taken to increase the durability of the building without loss of life against possible earthquakes that worry us as if it will happen at any moment.

We can list the methods of strengthening masonry structures, especially in terms of the material used, as follows;

- Reinforcement with reinforced shotcrete
- Strengthening with elastic Post-Tensioning straps
- Reinforcement with steel strips

- Strengthening with ready-made repair mortars
- Strengthening with curtain wall
- Strengthening with external curtain wall
- Reinforcement with cement injection
- Reinforcement with epoxy
- Strengthening with reinforced concrete horizontal and vertical beams
- Strengthening with tension bars
- Reinforcement with FRP and CFRP
- Strengthening with wooden posts, cross and buttresses

If we want to make an opinion about the applicability of these methods by referring to some of the reinforcement methods given above;

The first of these is the Reinforced Shotcrete Reinforcement Method, supported by the experiment conducted in the Gazi University Faculty of Technology Civil Engineering Structural Mechanics Laboratory. In the experimental studies, the strength values of three brick walls built with the same materials were measured against the out-of-plane repeated load. While no reinforcement was made on the first wall, the second wall was reinforced with shotcrete reinforced internally and the third wall internally and externally. Figure 10 shows the wall reinforced with internal and external wire mesh. The wall to be covered with steel mesh is shown in Figure 11. Figure 12 shows the

interior wall covering with steel mesh. Covering the outer surface of the wall with steel mesh is shown in Figure 13.

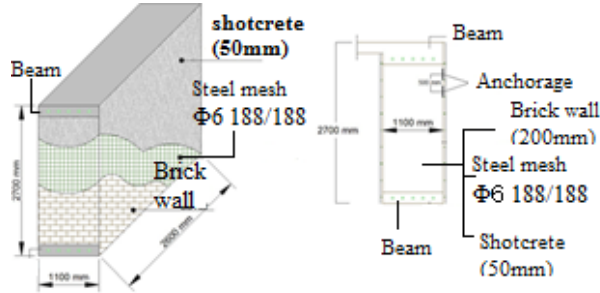


Figure 10. Wall reinforced with wire mesh internally and externally (Ateş, T.)



Figure 11. Wall to be covered with steel mesh (Ateş, T.)



Figure 12. Inner wall covering with steel mesh (Ateş, T.)



Figure 13. Covering the outer surface of the wall with steel mesh (Ateş, T.)

After the anchoring and bonding process of the mesh steels was completed, the wall surface was cleaned by blowing compressed air with a compressor. Later; With the ASE VP 500 TMK shotcrete machine shown in Figure 14, the wall surface was covered with shotcrete gradually from bottom to top.



Figure 14. Spraying the inner face of the wall with shotcrete
a) Preparation of concrete with ASE VP 500 TMK Shotcrete Machine b)
Application of shotcrete on the inner wall of the wall (Ateş, T.)

At the end of this process, the loading mechanism given in Figure 15 below was installed and the out-of-plane forces applied to the wall were applied, and the behavior of the walls against the earthquake effect was measured with LVDTs.

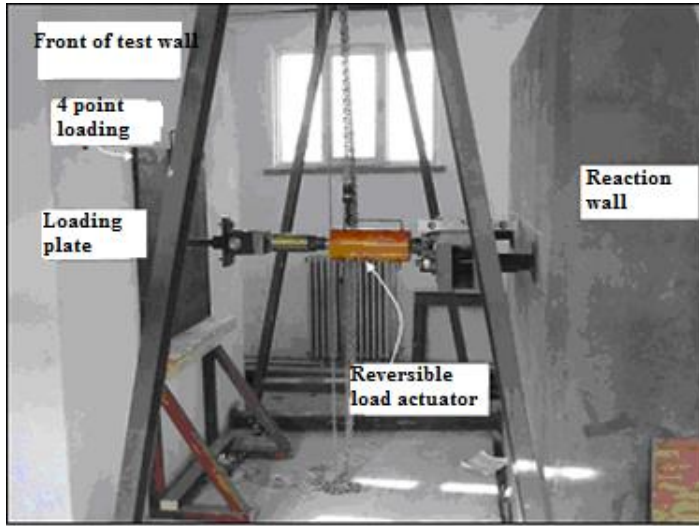


Figure 15. Loading mechanism (Ateş, T.)

One of the experimental results is given below;

- The maximum acceleration that the D_2 (reinforced internally and externally) wall can withstand without collapsing is calculated as $a_{D2} = 1.06$ g. This value is 4.56 times higher than the value of the D_0 (unreinforced) wall and 1.46 times the value of the D_1 (internally reinforced) wall.

Another interesting strengthening method is the strengthening method with Elastic Post-Tension strips. The changes in the behavior and strength of both masonry walls and masonry structures reinforced with used car tires were examined and they stated that a general idea on the structural behavior was reached. The most important of the analysis results, it has been shown that both strength and ductility increase with this strengthening method (Özen, G.Ö., Türer, A.). Preparation of Tires is shown in Figure 16. Tensioning Tires with Chock, Nut and

Nut is shown in Figure 17. Also, decorative solutions are given in Figure 18.



Figure 16. Preparation of Tires (Türer, A., Şimşek, Ç., Gölalmiş, M., Özden, B., Dilsiz, A., Özen, Ö., Korkmaz, H.)



Figure 17. Tensioning of Tires with Chock, Gijon and Nut (Türer, A., Şimşek, Ç., Gölalmiş, M., Özden, B., Dilsiz, A., Özen, Ö., Korkmaz, H.)



Figure 18. Decorative Solutions (Türer, A., Şimşek, Ç., Gölalmiş, M., Özden, B., Dilsiz, A., Özen, Ö., Korkmaz, H.)

In reinforcement with steel strips; this strengthening technique developed for damaged masonry structures can also be used to strengthen masonry structures that do not have sufficient earthquake safety. An example of steel strip arrangements in structures is given in Figure 19.



Figure 19. Steel Strip Arrangements (Altın, S., Kuran, F., Kara, M.E., Anıl, Ö.)

One of the methods used in masonry structures as well as reinforced concrete carcass structures is the repair and strengthening method called FRP (Fiber Reinforced Polymer) and CFRP (Carbon Fiber Reinforced Polymer), also known as Fiber Reinforced Composites (LTK), which has been widely used in recent years (Coşkun, E.). An example of reinforcing masonry wall with LTK is shown in Figure 20.



Figure 20. Strengthening the masonry wall with LTK (Coşkun, E.)

7. CONCLUSION AND DISCUSSION

With this study, Turkey lately as a result we live in an earthquake, especially low income of our people, they have built with an eye to the room and a roof of the hardship, I described it as lacking shelter from engineering services masonry drawing attention to the damage and destruction seen in masonry houses against earthquakes of these structures strengthening needs are revealed. However, by mentioning the techniques used in some reinforcement methods, which have been demonstrated by experimental studies in our universities, it can be observed that there are scientific studies on the strengthening of masonry structures in our country, but these studies are not applied in

these masonry structures due to both economic and information demand reasons. At least, it has been revealed that the necessary support and studies should be accelerated to apply these strengthening methods, which are found with valuable studies in our laboratories, to our buildings that have been attracted attention before possible earthquakes.

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CHAPTER 7

ENERGY STORAGE SYSTEMS AND TECHNIQUES

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1. INTRODUCTION

Nowadays, energy demand of human beings needed to meet their rising living standards has shown an increasing trend every passing day with regard to improvements in the technology and industrialization. Considering the gradual decrease of carbon-based fossil fuels and the negative effects of such fuels on the environment, increasing the efficiency of energy systems, promoting the use of renewable energy systems, as well as efficient storage of the generated energy have gain much attention in recent decades. Energy storage systems and methods have a potential to increase the efficiency of the energy used and to reduce the greenhouse effect and corespondingly present solutions to today's problems, such as global warming. This chapter consist of general information regarding energy storage systems and technologies and their comperisons to each other.

2. ENERGY and ENERGY STORAGE

Energy, which is generally defined as the potential to do work, has many different forms. According to the first law of thermodynamics, when a system and its environment are considered together, energy cannot disappear, but changes shape. Thanks to this feature of energy, energy storage systems can store the generated energy to be used when desired. On the other hand, when a comparison is made between energy generation methods, it is seen that energy is generally produced and used in the form of heat and electricity. Energy is generally divided into sections under the titles of generation, transmission, distribution and storage. While the first three of these deal with the shape change of

energy (electricity, chemical, heat energy, etc.), in the case of energy storage internal energy, kinetic energy potential energy and electric field energy etc. are mentioned [1,2].

Today, the generated electrical energy is used in two ways as alternative (AC) and direct (DC) current. Alternating current electrical energy is the electrical energy available in the network that can be transferred from where it is produced to another place, whereas direct current electrical energy is energy that can be stored through accumulator, batteries and cells. In this respect, energy efficiency can be increased thanks to systems that do not require a network to deliver electrical energy to consumers. Maintaining supply and demand balance in energy, making energy systems more efficient are some of the advantages of energy storage systems and methods [3]. Energy storage systems will become more efficient considering the following issues [4].

- Making energy systems more efficient,
- Ensuring integration in the use of renewable energy sources,
- Increasing domestic production and consumption in energy,
- Promoting the use of electrical energy,
- Facilitating access to energy (storage, etc.),
- Establishing stable systems by preventing fluctuations in grids, can be listed as. The benefits of energy storage systems are as follows [6, 7];
- Reduction of equipment capacity and more efficient use of equipment,

- Balancing supply and demand,
- Reduced initial investment, operation and maintenance costs,
- Reducing energy costs,
- Reduced emission values (CO₂, CFC),
- Flexible use of systems,
- Systems to be sustainable, reliable and economical,
- Improved indoor air quality despite increased heating / cooling performance.

The advantages of energy storage systems are evaluated from various aspects such as system integration, system control and system modeling, not by evaluating the selected storage system on its own [6]. Today, energy can be stored by taking advantage of its shape-shifting feature, not only by the use of batteries, accumulators and cells, but also by using many different technologies. Although this storage has different forms according to the technology used, it is a set of common techniques using different methods. The following are the main energy storage applications [5].

- Flywheel Energy Storage (FES),
- Pumped Hydropower Storage (Pressurized water storage, PSH),
- Compressed Air Energy Storage (CAES),
- Supercapacitors,
- Superconducting Magnetic Energy Storage (SMES),
- Thermal Energy Storage (TES),
- Hydrogen Energy Storage (HES),
- Batteries,

- Underground Thermal Energy Storage (UTES),
- Melt Salts,
- Chemical-Hydrogen Storage,
- Solid Media Storage,
- Ice Storage,
- Hot and Cold Water Storage,

A comparison of the above mentioned energy storage applications, different storage technologies and their basic characteristics is presented in Table 1. As can be seen from Table 1, energy storage is available for all energy forms.

Table 1. Comparison of different storage technologies and their basic features [1, 5]

Technological Method	Energy	Efficiency (%)	Cost (\$/kW)
Flywheel Energy Storage (FES)	Electrical	90-95	130-500
Pumped Hydropower Storage (PSH)	Electrical	50-85	500-4600
Compressed Air Energy Storage (CAES)	Electrical	27-70	500-1500
Supercapacitors (Ultra capacitors)	Electrical	90-95	130-515
Superconducting Magnetic Energy Storage (SMES)	Electrical	90-95	130-515
Thermal Energy Storage (TES)	Thermal	90-99	1000-3000
Hydrogen Energy Storage (HES)	Electrical	30-50	550-4500
Batteries	Electrical	75-95	900-3500
Underground Thermal Energy Storage (UTES)	Thermal	50-90	3400-4500
Melt Salts	Thermal	40-93	400-700
Chemical-Hydrogen Storage	Electrical	22-50	500-750
Solid Media Storage	Thermal	50-90	500-2000
Ice Storage	Thermal	75-90	6000-15000
Hot and Cold Water Storage	Thermal	50-90	300-600

3. ENERGY STORAGE SYSTEMS and TECHNIQUES

In Figure 1, commonly used energy storage techniques are classified according to energy form. Unlike these classifications, it is possible to make different classifications according to energy input and output or energy conversion process [7].

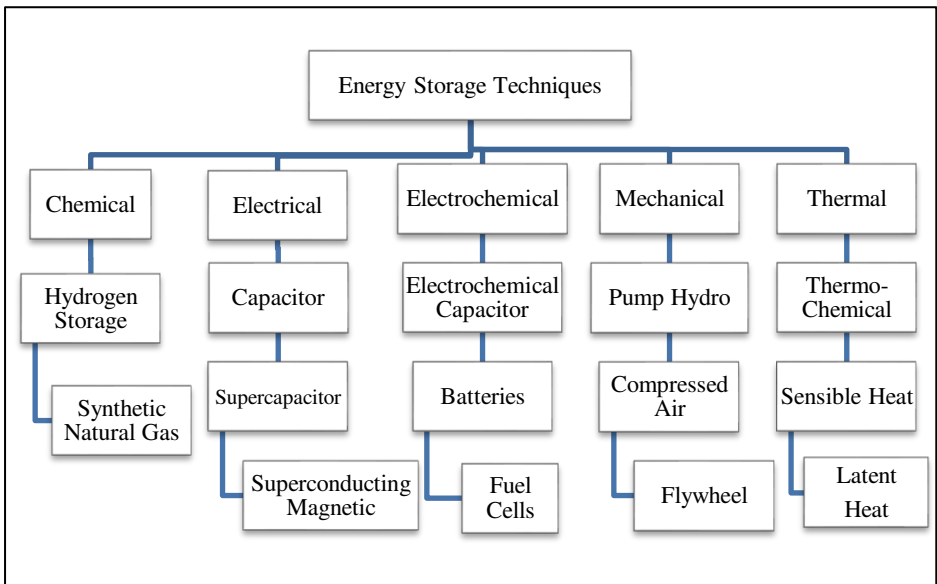


Figure 2. Energy storage techniques [7]

Electrical energy derived from renewable energy source systems is usually used where they are produced. Due to changes in resources and demand during the day/night or summer/winter periods, different types of storage alternatives are integrated into these systems and used. In addition to on-site production, storage and usage processes, the surplus energy produced may need to be transported to different regions or stored in different forms and waiting as potential energy for long periods. Among the things that can be done in this regard is the storage

of energy in portable form as synthetic fuel. In this case, called Power-to-Fuel, excess energy from edible or traditional power generation systems is used in the production of synthetic fuels. In Figure 2, the stages of ammonia production from power - fuel, power - hydrogen and power - integrated into various power generation systems are schematically presented. The most effective solution to obtain fuel artificially and chemically is to synthesize carbon dioxide (CO_2) gas with water (H_2O). This transformation technology is also called "artificial photosynthesis" due to its chemical similarity. Hydrogen produced by electrolysis can be stored directly, as well as evaluated in different sectors by using it in ammonia production. Energy storage by obtaining fuel from power allows flexible use of energy in different sectors such as transport, agriculture, chemical production or re-energy production in accordance with demand [7].

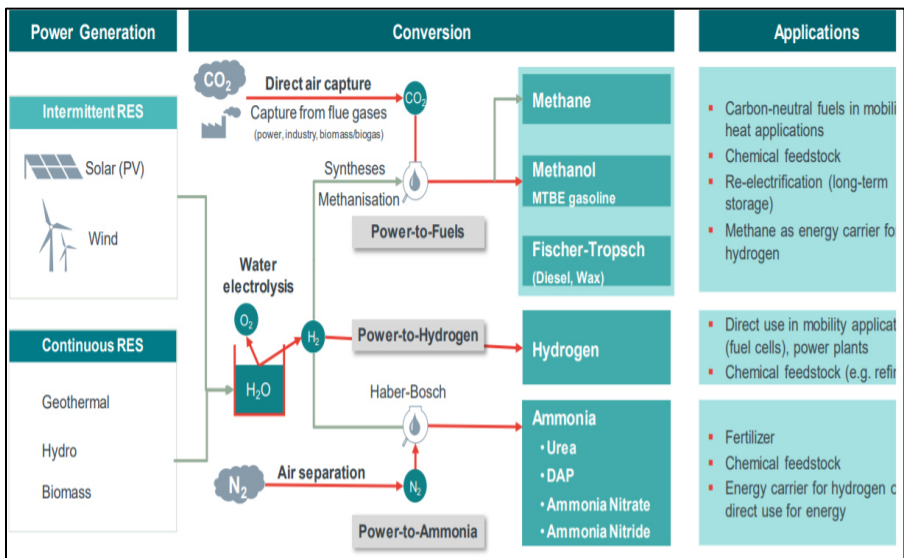


Figure 2. Conversion of renewable power into various forms of chemical energy carriers [8]

3.1 Electro-Chemical Energy Storage Systems

3.1.1 Rechargeable Batteries

A. Advanced Lead Acid Batteries; these batteries are the advanced of traditionally used batteries. These batteries use lead as anode, lead dioxide as cathode and sulfuric acid as electrolyte. Such batteries are suitable for fixed storage uses [9].

B. Flow Batteries; they are used in fixed storage systems with capacities between 1 kWh-10 MWh. Such batteries are currently being developed [9].

C. Lithium-Ion Batteries; the biggest advantages of these widely used batteries are their high-energy storage capacity, low internal resistance and efficiency of over 90%. Their efficiency decreases when they are exposed to high temperatures. Their useful life starts to decrease as of the date of manufacture, which shows the disadvantages of such batteries.

D. Metal - Air Batteries; because these batteries use oxygen as cathode and metals such as magnesium, iron or lithium as anode, they have a more economical and high-energy efficiency than lithium-ion batteries. Despite this, it is among the batteries that are being developed today [9].

E. Sodium Batteries; as an electrode, they are batteries made of sodium or its compounds. This of type batteries commercial use is common.

F. Nickel Cadmium Batteries; Such batteries have a nickel electrode and a cadmium electrode in the aqueous potassium hydroxide electrolyte. They are not preferred because of their low efficiency (around 75%). It can be used in many areas such as emergency lighting, telecommunication, solar energy systems [10].

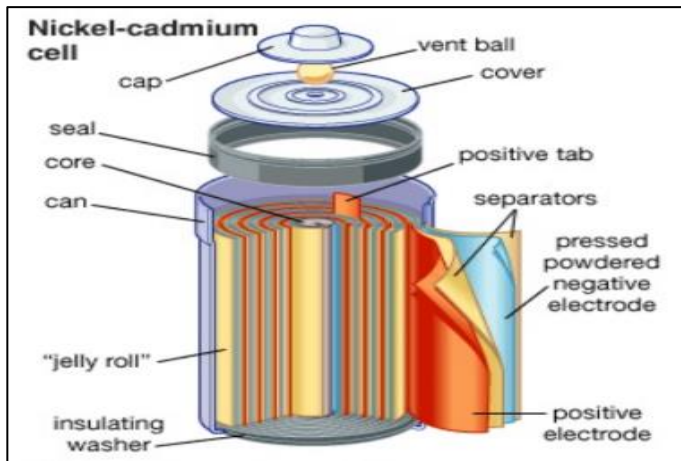


Figure 3. Nickel-cadmium cell [11]

3.1.2 Fuel Cells

Fuel cells, such as batteries, do not contain fuel and its burners in their bodies. They constantly receive these two chemicals from a stored external source. Hydrogen, or direct hydrogen, obtained from alternative sources with the help of a fuel converter, is an energy-producing device that reacts with oxygen. They have advantages such as not causing environmental and noise pollution, not containing moving parts, and obtaining more energy conversion than fossil fuels. Such batteries have an efficiency of up to 40-60%, depending on the type of fuel cell. While fuel cells create a higher value than batteries in

terms of specific energy value, they have a worse value in terms of specific power [12].

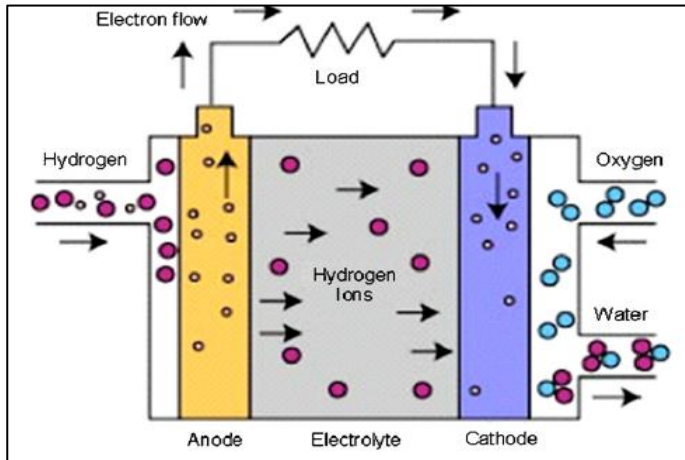


Figure 4. Schematic representation of the operating principle of a fuel cell [13]

In addition, there are many types of fuel cells. Fuel Cell (AFC), Polymer exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), Solid Oxide Fuel Cell (SOFC) are. The main differences between these types of batteries are the electrolyte used, operating temperature, design and application areas [13].

3.2 Mechanical Energy Storage Systems

It is based on the principle of storing the energy created by the force acting on a material. There are two basic systems for storing the energy generated by the applied force. While the first of these is related to the change in potential energy, the second is related to kinetic energy.

While these two energies can be transformed between themselves, they can also be transformed into heat energy or work [14].

3.2.1 Flywheel Energy Storage Systems

Flywheel energy accumulators consist of specially designed brackets placed in a housing at very low pressure to reduce self-discharge losses from a flywheel with a single piece or composite structure combined with an engine generator [15]. Flywheels are often used in power systems in the transportation, telecommunications, and nuclear research industries to provide controlled power, to obtain large amounts of power. However, the amount of energy accumulated in flywheels is very low compared to pumped water and compressed gas methods. In this regard, flywheels are not preferred as energy storage systems in large-scale enterprises. In this respect, flywheels are systems used for short-term storage of low amounts of energy.

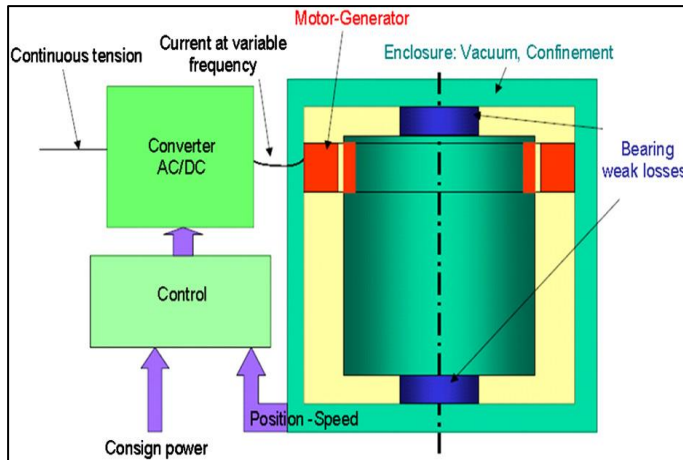


Figure 5. Flywheel energy accumulators [16]

3.2.2 Compressed Air Energy Storage Systems (CAES)

CAES systems are defined as systems that store energy as compressed air in underground caves [17]. These systems use the electrical energy to be generated to move compressors. In addition, they use this air stored under pressure in a piston or turbine to meet their energy needs when necessary. Compressed air for CAES systems is stored in geological structures such as underground water layers, abandoned salt or other mineral deposits. In practice, the smallest CAES energy storage unit has a power of 10 MW and a power generation of 100 MW/s. Compressed air energy storage systems have higher power and energy density compared to pressurized water storage systems [18].

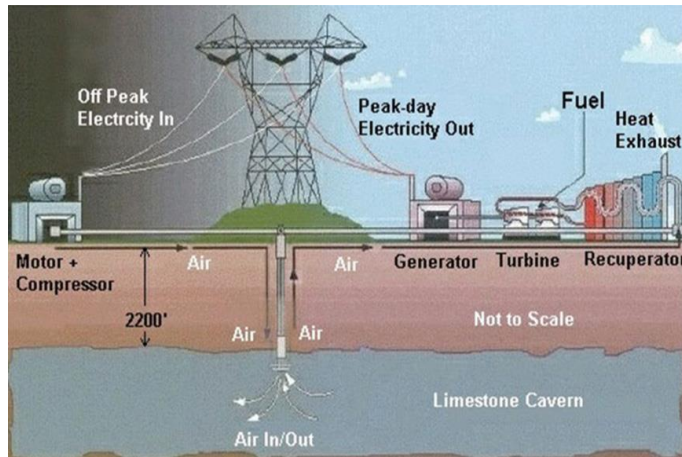


Figure 6. Illustration of compressed-air energy storage [19].

3.2.3 Pumped Hydro Storage Systems (PHS)

The biggest advantage of this technology is that it is easily obtainable. It is based on the principle of using the power of water from highly concentrated renewable energy sources. Today, it is often used in applications requiring high power (100MWh-10GWh). These systems have two reservoirs. When the demand for electrical energy is at low values, potential electrical energy is accumulated by storing water from the Lower Tank to the upper tank thanks to the electrical energy stored in pumped storage sub-transmission stations. At times when demand is intense, movement is given to turbines that generate electric energy by using the power of the water flowing out of the upper reservoir. These systems have a conversion efficiency of approximately 65-80%, depending on equipment characteristics [20]. In addition, a 1-ton body of water falling from a height of 100 meters produces 0.272 kWh of

electrical energy. The disadvantages of these systems are that they need production sites that cover large areas [20].

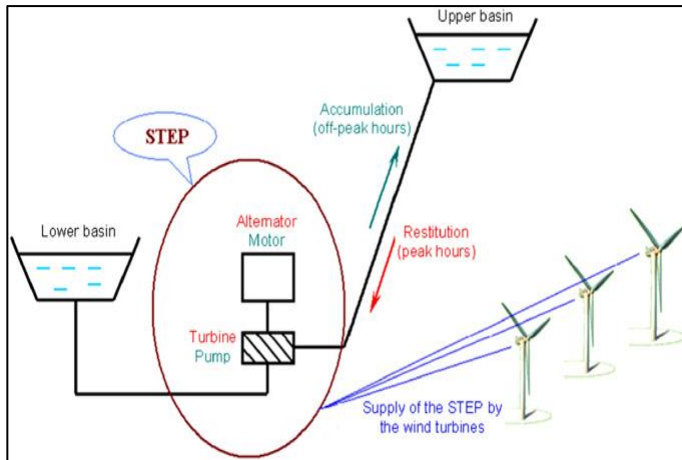


Figure 7. Schematic representation of an example hydro warehouse [21]

3.3 Thermal Energy Storage Systems (TES)

There are two different thermal storage mechanisms. The first is the energy that solid and/or liquid materials store in their bodies with an increase in temperature. The other is heat storage, which causes the phase change of materials without chemical changes [14]. Thermal energy storage allows hot or cold to be stored for later use, while helping to balance the temperature, time, place, or power difference between energy production and consumption in the context of supply and demand [22]. Therefore, thermal energy storage can be used for hot or cold or both storage according to needs. For thermal storage, waste heat of a power plant, solar energy and geothermal energy, etc. it needs heat source systems such as [9].

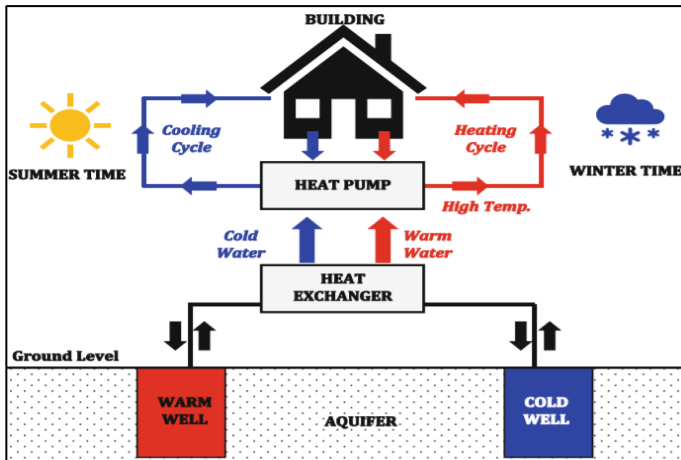


Figure 8. Schematic representation of a heat pump TES system [23]

3.4 Electrical Energy Storage Systems

Capacitors are two-pronged circuit elements that store electrical energy as an electric field. It is obtained by placing an insulating agent between two conductive plates. Energy can be stored in these capacitors in an electric field in a reversible way. There are two general types of devices in this regard and they have a very wide range of uses according to practical usage characteristics such as the amount of energy they store, energy absorption and oscillation values [14].

3.4.1 Superconducting Magnetic Energy Storage Systems (SMES)

SMES systems store energy by a superconducting magnetic coil dipped in a very cold liquid, such as liquid helium, contained in a very well insulated bottle [24]. The resistances of superconducting magnetic coils are zero, so the electric current will not decrease over time once it starts flowing. Coils are not very large in size [25]. In SMES, power is stored by magnetic rotation of DC electric current in the coil. This process is

stopped by doing the opposite. The advantages of SMES systems are efficient, robust, reliable and quiet operation, and their efficiency is around 90%. Disadvantages of SMES systems are that they need cooling are hypersensitive to high cost and temperature [25].

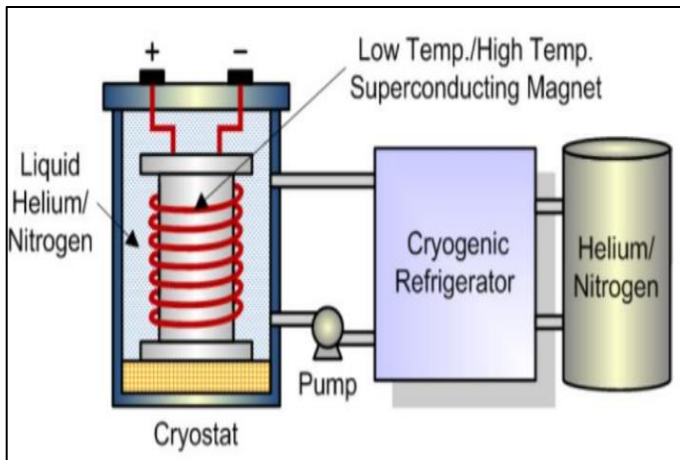


Figure 9. Super magnetic energy storage (SMES) system design [26]

3.4.2 Supercapacitor Energy Storage Systems

These components have the characteristics of both capacitors and electrochemical batteries, but they do not exhibit a chemical reaction that greatly increases cyclic capacity. Energy storage in supercapacitors is done in the form of an electric field formed between two electrodes [20]. Supercapacitors, when compared to commonly used capacitors, are capacitors with a high energy density. They have a much longer life than batteries. Compared to batteries, although they have a lower energy density, their power densities are several times higher than those of the batteries [27].



Figure 10. Super capacitors assembled in series [28]

3.5 Chemical Energy Storage Systems

Chemical reactions can absorb or release significant amounts of energy. In this way, chemical bonds break or form new substances. Chemical fuels such as coal, gasoline, diesel fuel, natural gas, and liquefied petroleum gas (LPG), propane, butane, ethanol, biodiesel and hydrogen are the fuels that can be used to store energy. This process is known as power-gas or power-liquid, depending on the phase of the output chemical fuels. Fuels, chemical, industrial, mechanical power or thermal energy in commercial or residential applications store large amounts of energy to produce the energy to move long distances or for longer periods, are widely used. Figure 11 shows a comparison of the

energy densities (in MJ per unit volume) of commonly used chemical fuels and batteries [23, 29].

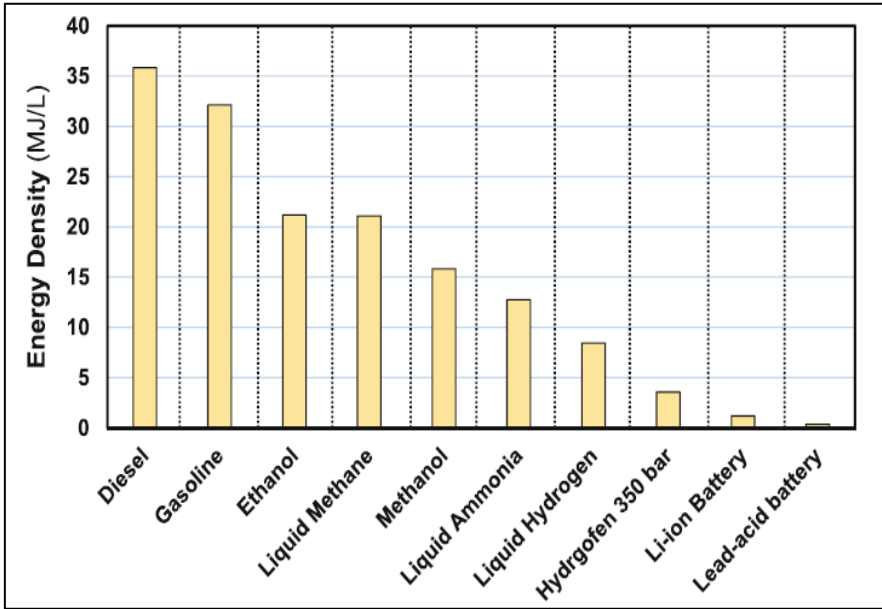


Figure 11. Comparison of the energy densities of chemical fuels [28]

Storage of electrical energy in chemical form through electrolysis in the case of hydrogen is compatible with electrochemical storage, as chemical fuels have higher energy densities. Hydrogen is not a direct source of energy; instead, it is an intermediate form of energy and is an ideal candidate as an energy carrier or storage medium. A conceptual flow chart of a hydrogen energy storage unit is given in Figure 12. Here, excess electrical energy generated from a renewable source, such as solar, wind, or any other source, is used and stored to produce hydrogen. Stored hydrogen can be used in turbines or fuel cells to generate electrical energy, depending on demand. In the current flow chart,

hydrogen production is accomplished by water electrolysis. However, in the case of electrolysis, the round-trip conversion efficiency of such an application is not higher than 35%.

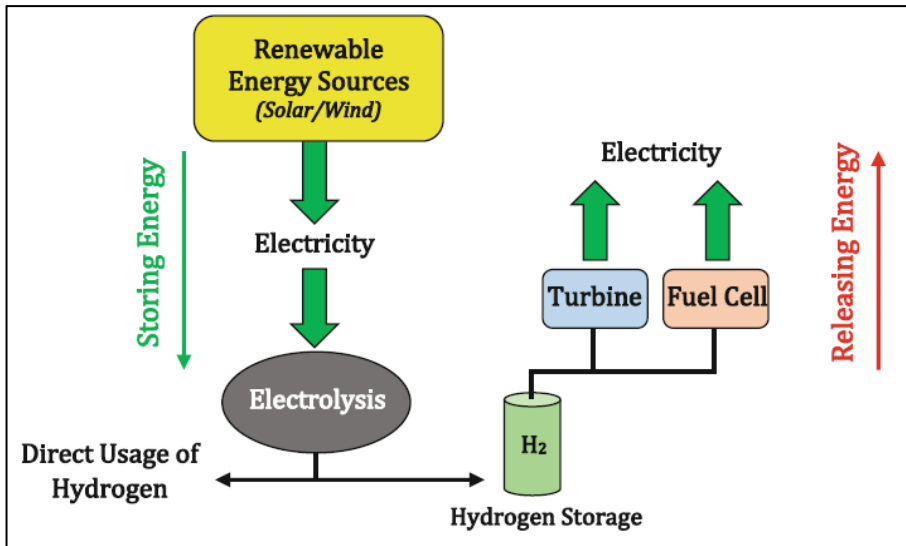


Figure 12. Hydrogen energy storage system [23, 30]

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CHAPTER 8
ENERGY STORAGE VIA HYDROGENATION OF CO₂ TO
HYDROCARBONS

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1. INTRODUCTION

It is a well-known fact that the rapid growth of the population and the improvements in the industry have rapidly increased the energy needs of countries [1]. The most common known and serious anthropogenic activity resulting in the greenhouse effect is that burning of fossil fuels in the power plants to generate electrical energy which is one of the most basic needs of humanity. The release of high concentrations of greenhouse gases (GHGs), such as carbon dioxide (CO_2), methane (CH_4), chlorofluorocarbons (CFCs) and nitrous oxide (N_2O) to the atmosphere from the stack of the power plants can be considered as the most remarkable cause for global warming [1-5]. These high emissions have considerably led to the increase in the atmospheric temperature resulting in various negative impacts on earth, like increasing sea level, and loss of biodiversity [6-7]. To mitigate greenhouse gas emissions, the most outstanding options can be listed as the usage of CO_2 capture and storage technologies and improvements in energy efficiency and correspondingly decrease in the energy demand [2, 6, 8-10]. Hydrogenation of CO_2 to hydrocarbons, such as methane and methanol that is one of the most significant potential storage media, storing the electric energy into an easy transportable and liquid fuel, can also be regarded as the most promising technique in CO_2 conversion [11]. Liquid fuels generated from CO_2 conversion using H_2 plays an important role as a source that does not release CO_2 emissions like hydroelectric, solar or nuclear energy [12]. In this context, this chapter aims to explain conversion of CO_2 to hydrocarbons more specifically to methanol contributing to energy storage and providing the reduction

in the concentration of CO₂ in the atmosphere via hydrogenation. It will briefly give an idea about energy storage based on conversion of CO₂ into hydrocarbon and methanol using H₂ and explain system performance as well as factors having an impact on hydrocarbon selectivity and yield.

2. CARBON DIOXIDE CAPTURE TECHNOLOGIES

There are several technologies proposed for carbon capture based on pre-combustion and post-combustion options [1, 4, 6]. Absorption, adsorption, cryogenic distillation and membrane processes are techniques mostly preferred CO₂ capture as shown in Figure 1 [2, 6-7].

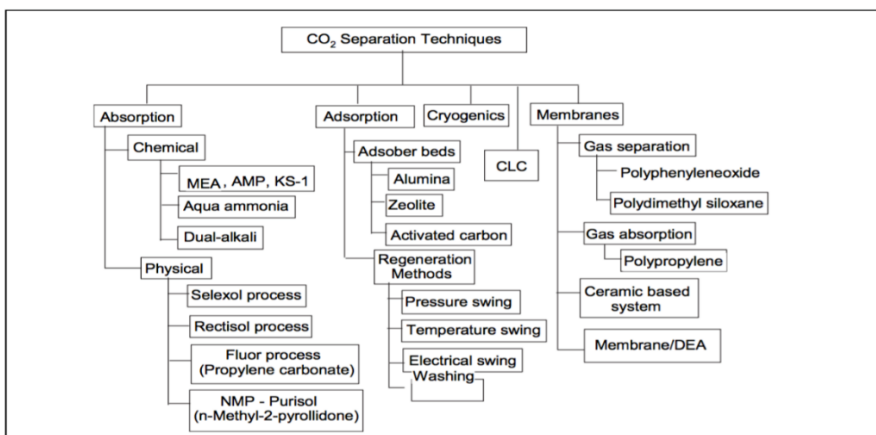


Figure 1. Conventional CO₂ capture technologies, in which CLC is Chemical Looping Combustion [3, 13].

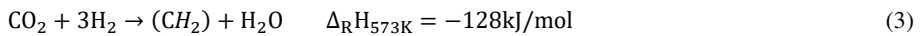
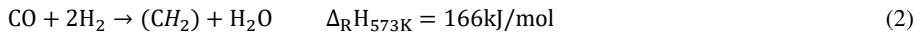
Among these technologies, the absorption process presenting the highest removal efficiency is generally preferred to separate CO₂ from flue gas in conventional gas-liquid contactors [7]. CO₂ separation from flue gas by chemical absorption process using aqueous amine solutions has been used since 1930s [14-16]. Due to some disadvantages of

amine-based absorption technology, such as low CO₂ loading, high corrosivity and toxicity, researchers have focused on techniques presenting higher CO₂ absorption capacity and minimizing operating and investment costs and finally having more environmental-friendly approach [1, 3, 17]. To cope with these issues of conventional gas absorption techniques, membrane technologies based on gas separation and gas absorption can be considered as a promising method because of their operational and economical advantages, such as independent gas/liquid control, flexible operation, optimal load of the absorption liquid, very compact equipment, low investment costs and low pumping power for the absorption liquid [18]. As for the reduction in the increasing amount of CO₂ in the atmosphere by hydrogenation reaction, it has been accepted as one of the most important chemical conversions of CO₂ providing a vital contribution to sustainable development in the energy and environmental sectors. The main products of CO₂ conversion by hydrogenation are commonly identified as methanol and hydrocarbons employed as fuels in internal combustion engines and stored and transported [19]. Therefore, synthesis of hydrocarbons and methanol will be separately explained in following parts of this Chapter.

2.1 Hydrocarbon Synthesis based on CO₂ Conversion by Hydrogenation

Carbon dioxide can be hydrogenated to hydrocarbons either by direct reaction that is similar to Fischer-Tropsch synthesis including conversion of carbon monoxide (CO) to hydrocarbons or indirect

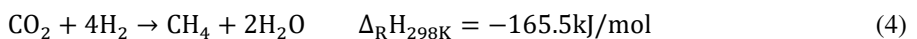
reaction based on the multi-step transformation as presented in the following Eqs. (1) - (3) [19].



The modified Fischer-Tropsch (H_2/CO_2) mechanism is implemented with several metal based catalysts, such as iron that has been promoted with potassium, copper, manganese, aluminum oxide [12, 19]. The mechanism describing hydrogenation of carbon dioxide to hydrocarbon is presented in Figure 2. The first attempt to reduce CO_2 is carried out by iron (II) and then H radical that is free on the catalyst reacts with carbonyl C to form OH formic acid and CO, respectively. Similarly, Fe- CH_2 radical also produced during conversion of CO_2 to hydrocarbon by hydrogenation process [19].

Along with some operating conditions, such as space velocity, temperature and pressure, the effects of catalyst type, such as role of active site and role of promoter on H_2/CO_2 to hydrocarbon have been investigated in numerous studies. Results in the literature emphasized that both catalyst type and the reactor configuration that should possess higher activity and selectivity have a vital impact on hydrogenation of CO_2 to hydrocarbon [19].

The simplest conversion of hydrogen and CO_2 into a hydrocarbon as shown in the following Eq. (4) is the Sabatier reaction discovered by French chemist Paul Sabatier in 1910 [20].



Since Sabatier reaction has some drawbacks, such as the excessive consumption of H_2 , lower energy per volume and more difficult storage compared to methanol, it can be regarded as inappropriate way to convert CO_2 to fuels via hydrogenation [19]. The main product of this reaction, methane is commonly called as synthetic natural gas (SNG). This exothermic reaction is implemented onto metal based catalysts including Co, Ni and Ru as the active phase [20].

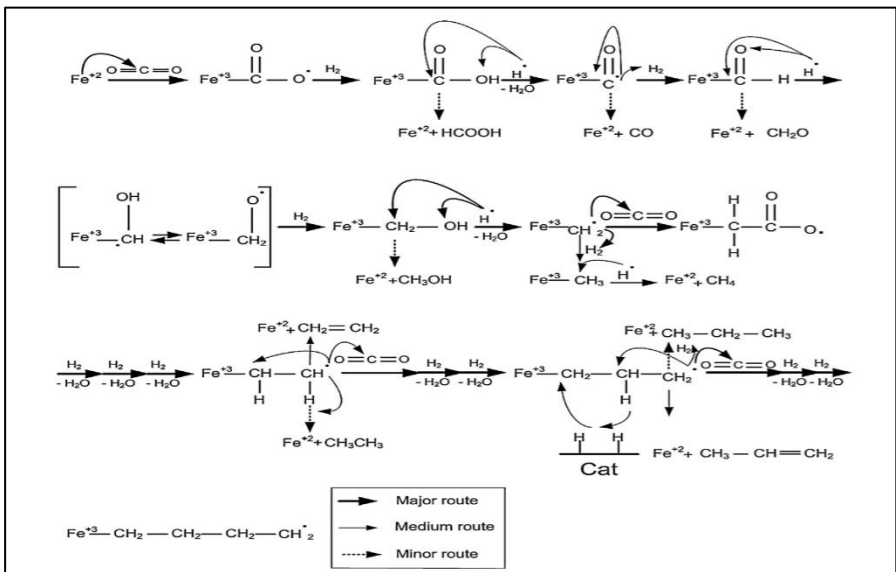
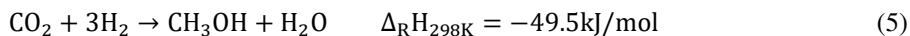


Figure 2. Overall reaction mechanism of CO_2 hydrogenation [19].

Sabatier reaction is based on the reaction with H_2 over a metal, such as nickel and ruthenium that are generally preferred to catalyze methanation reactions. Some applications for this type of reaction are purification of H_2 using to manufacture ammonia, gas chromatograph detectors converting CO and CO_2 to CH_4 to obtain more sensitive results [21].

2.2 Methanol Synthesis based on CO₂ Conversion by Hydrogenation

Methanol that is a general solvent used as an alternative fuel can be produced by reaction between CO₂ and H₂ in optimum conditions including low reaction temperature and high reaction pressure supporting methanol synthesis [19].



Even if this reaction is less exothermal than the Sabatier reaction, its exothermic property requires a good temperature control mechanism considered as an issue stemming from methanol production [11]. In accordance with literature, common metal based catalysts used in the conversion of CO₂ to methanol via hydrogenation are Cu and Zn along with other metals Zr, Ga, S, Al, B, Cr, Ce, V, Ti used as a promoter. The CO₂ conversion based on methanol production is generally implemented with a ternary Cu-Zn-Al oxide catalyst. Optimum operating conditions needed for the implementation of this CO₂ hydrogenation reaction can be listed as pressure between 5 and 10 MPa and temperature in the range of 473-523 K [22]. An example for the reaction mechanism to generate methanol from CO₂ hydrogenation with bifunctional catalyst including Cu and ZrO₂ is presented in Figure 3.

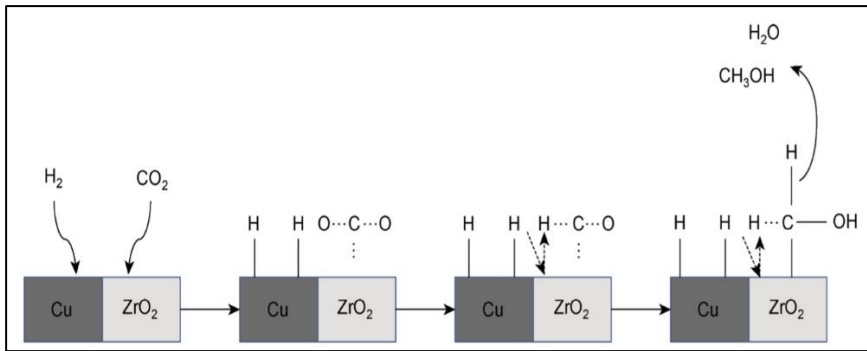


Figure 3. Reaction mechanism of CO₂ hydrogenation based on methanol production via Cu/ZrO₂ bifunctional catalyst [22].

Overall process associated with methanol production from CO₂ hydrogenation is often referred as green methanol synthesis owing to the reduction in the release of CO₂ emissions into the atmosphere since the renewable energy in the H components of the molecule represent around half of its heat of combustion [23].

3. ENERGY STORAGE SYSTEMS

Energy storage means a formation of energy in different ways to be used to carry out some processes in the future. In this context, the energy which can be stored and transported has gained much attention for many years. Electrical energy which can not be stored requires the transformation of energy into the another form of energy to provide its storage. Energy storage methods can be divided into 5 groups: i) chemical energy storage including hydrogen, biofuels, thermo-chemical energy storage, ii) electrochemical energy storage consisting of primary/secondary cell or battery, reserve cell and fuel cell, iii) electrical energy storage comprising capacitor, supercapacitor and superconducting magnetic energy storage, iv) mechanical energy

storage including flywheel system, pumped hydro storage system (PHSS), compressed air energy storage (CAES) system, v) thermal energy storage consisting of sensible heat system, latent heat system, absorption and adsorption system. These methods show significantly differences in accordance with their usage area. Energy storage system can be adapted to varying status resulted from consumer's behavior and stemmed from new technologies. The fundamental issues related to energy storage that are to provide a sustainable and environment-friendly approach are brought to mind providing the diversity in the energy sources and increasing the usage of renewable energy [24].

Energy storage systems classified above have some drawbacks, such as limited capacity, low energy density. Power to hydrogen includes the most significant stage for chemical energy storage. The hydrogen is generated from water splitting thanks to electric energy stemming from excess renewable energy. This approach is implemented with electrolyzers producing hydrogen and oxygen. However, the direct conversion of hydrogen and carbon dioxide to the end products can be preferred because of the fact that hydrogen storage is not cost-effective [20]. This chapter focuses on energy storage in the form of hydrocarbons, such as methane and methanol coming from CO₂ conversion by hydrogenation. Moiola and coworkers (2019) investigated energy storage in the form of methane and methanol from hydrogenation of CO₂. They found that methanol was a better option to carry the energy than methane because of some causes consisting of the lower energy losses in the production process and the liquid form at ambient conditions. In accordance with their results the methanol and

methane stored the hydrogen energy as 85.3% and 78.2%, respectively under ideal circumstances without energy losses. When production processes of methane and methanol based on CO₂ conversion via hydrogenation are compared, methanol production has some issues resulting from the energy requirements of upstream and downstream processes. They improved hybrid energy storage system using a commercial Cu/ZnO/Al₂O₃, that is widely used in the literature as a catalyst, to synthesize methanol showed high energy storage potential [20].

Bos and Brillman (2015) developed a new condensation reactor that is used in the conversion of CO₂ to methanol to obtain better storage capacity for renewable electric energy. This novel design includes two temperature zones including a cold condensation zone in the top of the reactor and a hot reaction zone in the bottom of the reactor providing in situ condensation of the products vapors at low pressure and so to shift the equilibrium. They used a commercial Cu/ZnO/Al₂O₃ as a catalyst. They found that a remarkable methanol production without forced convection. The important output from the study was related to the energy efficiency that was too low to produce methanol with a positive energy balance [11].

Zhang and co-workers (2012) investigated the effect of promoter including SiO₂, TiO₂ or mixture of them on the performance of CuO-ZnO-Al₂O₃ catalyst to synthesize methanol from CO₂ conversion via hydrogenation. They found that the promoted catalyst including SiO₂-TiO₂ showed a higher methanol selectivity (41.17%) than that of a

catalyst without promoter (23.32%). CuO-ZnO-Al₂O₃ catalyst promoted with SiO₂, TiO₂ or SiO₂-TiO₂ showed better catalytic performance than the one without promoter. Promoters contributed to the increase in CO₂ conversion rate and methanol yield. When promoters were compared in terms of their performance, promoter SiO₂-TiO₂ showed better results than SiO₂ or TiO₂ causing a weaker acid strength and a higher acid concentration on the surface of the catalyst [25].

This chapter briefly explains energy storage system based on CO₂ conversion to methanol and hydrocarbon by hydrogenation process, gives some examples for factors affecting the system performance, such as type of the catalyst, usage of promoter, type of the reactor. Also, it includes some issues regarding the exothermic reaction needed for a temperature control during the production of methanol.

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