MARMARA UNIVERSITY

INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

THEORETICAL AND EXPERIMENTAL INVESTIGATION OF CO-GASIFICATION AND CATALYTIC GASIFICATION

BEYZANUR ÖZTÜRK

MASTER THESIS

Department of Chemical Engineering

Thesis Supervisor

Asst. Prof. Dr. Uğur ÖZVEREN

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Beyzanur ÖZTÜRK, a Master of Science student of Marmara University Institute for Graduate Studies in Pure and Applied Sciences, defended her thesis entitled **"Theoretical and Experimental Investigation of Co-Gasification and Catalytic Gasification"**, on..... and has been found to be satisfactory by the jury members.

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APPROVAL

Marmara University Institute for Graduate Studies in Pure and Applied Sciences Executive Committee approves that Beyzanur ÖZTÜRK be granted the degree of Master of Science in Faculty of Engineering, Chemical Engineering Program on 19.02.2020 (Resolution No: 2020/07-02)

Director of the Institute
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January, 2020 **Beyzanur ÖZTÜRK**

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KATALİTİK VE BİRLİKTE GAZLAŞTIRMANIN DENEYSEL VE TEORİK İNCELENMESİ

Birlikte gazlaştırma ve katalitik gazlaştırma işlemi, reaksiyon hızını arttırıp çalışma sıcaklığını düşürürerek genel sistemin enerji verimliliğini arttırmak için uygundur. Bununla birlikte, bir termal dönüşüm olarak birlikte gazlaştırma ve katalitik gazlaştırma, fiziksel özelliklerin değiştiği, ısı ve kütle transferi gibi çeşitli kimyasal ve fiziksel süreçleri içeren karmaşık işlemler olarak düşünülmektedir.

Bu tez, biyokütle, kömür ve bunların karışımları için birlikte gazlaştırma ve katalitik gazlaştırmanın sinerjik etkileşimlerinin teorik ve deneysel olarak belirlenmesini amaçlamaktadır. Bu çalışmada Fındık Çotanağı, Çan Kömürü ile bunların karışımları, NETZSCH 449 Jüpiter F3 termogravimetrik analiz cihazı ile katalitik ve katalitik olmayan koşullar altında CO_2 gazlaştırma kullanılarak gazlaştırıldı. Termogravimetrik analiz verileri yardımıyla, izotermal olmayan kinetik analizler, sırasıyla Friedman ve Flynn-Wall-Ozawa (FWO) diferansiyel ve integral eş dönüşüm yöntemleri kullanılarak gerçekleştirildi. Kinetik sonuçlar katalitik etkinin belirlenmesi için kullanıldı. Ayrıca, sinerjistik etkileşimlerin belirlenmesi için, Aspen Plus® yazılımında geliştirilen akışkan yataklı gazlaştırıcı kullanılarak teorik çalışma yapıldı. Aspen Plus®'taki simülasyonlardan elde edilen sonuçlar ile literatürden elde edilen deneysel sonuçların iyi bir uyum içinde olduğu doğrulandı ve bu nedenle Aspen Plus®'taki modelin, singazın bileşimini ve ekserji değerini doğru olarak tahmin etmek için kullanılabileceğini gösterdi.

Anahtar Kelimeler: Termal Analiz, Kinetik, Akışkan Yatak Gazlaştırıcı, Aspen Plus®, Birlite Gazlaştırma, Katalitik Gazlaştırma

ABSTRACT

THEORETICAL AND EXPERIMENTAL INVESTIGATION OF CO-GASIFICATION AND CATALYTIC GASIFICATION

Co-gasification and catalytic gasification are suitable to enhance overall system energy efficiency by increasing reaction rates and reducing operating temperature. However, co-gasification and catalytic gasification as a thermal conversion is thought of complex phenomena that involve several chemical and physical processes like alteration of physical properties and chemical reactions including heat and mass transfer.

This dissertation aims to investigate theoretical and experimental determination of synergistic interactions of co-gasification and catalytic gasification for biomass, coal and their blends. Therefore, in this study, hazelnut husk, Çan lignite and their blend were gasified in NETZSCH 449 Jupiter F3 thermogravimetric analyzer under catalytic and non-catalytic conditions by CO_2 gasification. By the aid of thermogravimetric analyzer data, the non-isothermal kinetic analysis was conducted by using differential and integral isoconversional methods; Friedman and Flynn-Wall-Ozawa (FWO) method, respectively. The kinetic results were used for determination of catalytic effect. Furthermore, theoretical study was performed by using fluidized-bed gasifier in the Aspen Plus® software to determinate synergistic interactions. The validation results obtained from simulations in Aspen Plus® depicted a good agreement with the experimental results from literature, so the demonstration of the model in Aspen Plus® can be employed to predict the composition and exergy value of syngas accurately.

Keywords: Thermal Analysis, Kinetics, Fluidized-bed gasifier, Aspen Plus®, Co-gasification, Catalytic Gasification

SYMBOLS

α **:** Degree of conversion

C **:** Carbon

Ea : Activation energy (kJ/mol)

GJ : Giga Joule

f(α) : The reaction model (function of conversion)

H **:** Hydrogen

kg : Kilogram

mg : Miligram

Mt : Megaton (1000000 tons)

n : Degree of reaction

MJ : Mega Joule

N : Nitrogen

O : Oxygen

R : Boltzmann gas constant (8.314 J $mol^{-1} K^{-1}$)

S **:**Sulphur

t **:** Time (s)

T **:** Temperature (°C)

ABBREVIATIONS

A **:** Ash

ASTM **:** American Society for Testing and Materials

CFB **:** Circulating Fluidized Bed

ETC **:** Et Cetera

EÜAŞ **:** Electric Generation Corporation

EPDK **:** Energy Market Regulatory Authority

FC **:** Fixed Carbon

FWO **:** Flynn Wall Ozawa

IEA :International Energy Agency

MTA **:** Mineral Research and Exploration Institute

MTOE **:** Millions of Tonnes of Oil Equilavent

M **:** Moisture

Min **:** Minute

TFC **:** Total Final Consumption

TG **:** Thermogravimetry

TGA **:** Thermogravimetric Analysis

TKİ **:** Turkey Coal Institution

TTK **:** Turkish Hard Coal Enterprise Intstitution

VM **:** Volatile Matter

WT. % **:** Percentage (Weight Basis)

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1. INTRODUCTION

Energy is a significant factor considering improvement of living standards and countries economic and social development. While there are major developments and alterations in the industrial field in the world, the increase in the population on the other hand increases the energy demand.

Blends of coal and biomass for co-gasification is considered as a promising method from the point of improved efficiency, environmental and economic benefits [1]. CO_2 assisted gasification increases the product gas lower heating value. Furthermore, the utilization of catalytic properties of compounds, that naturally exists in biomass, affecting the CO_2 gasification process and can even promote higher thermochemical reactivity in biomass blended coal compared to solely coal [1, 2]. Recently, important researches related to co-gasification of various coal and biomass blends are performed [3]. Extensive studies on co-gasification are available in the literature [4]. However, there are limited studies have been reported on catalytic and non-catalytic co-gasification of blended coal and biomass under CO_2 atmosphere.

The objective of this study is to investigate catalytic and non-catalytic CO_2 assisted co-gasification of Çan lignite and hazelnut husk by using thermal analysis to determine the underlying kinetics in comparison to the parent lignite and biomass. Moreover, this study presents the novelty of simulating catalytic and non-catalytic co-gasification under CO2 atmosphere for determination of synergistic interactions, sensitivity analysis was conducted by using fluidized-bed gasifier generated by using Aspen Plus® software.

1.1. Energy

After the industrial revolution with developing industry, energy has been used in all areas of life. Deficiency of energy in the world means low living standards for developed countries and poverty for developing countries. Therefore, alternative energy resources and new technologies to use energy resources efficiently have been investigated due to high energy consumption in 20^{th} century.

The growth in world population with increasing urbanization, and industrialization have made energy technology more critical in all areas of human life such as industry, residantal, commercial and public services, transport etc. Because of exhausting energy

resources, foreign dependency and environmental effects, producing safe, adequate, cheap and clean energy is among the main economic and social problems of the countries.

Energy resources can be classified into nonrenewable and renewable. Nonrenewable energy resources, like coal, natural gas, and petroleum (oil), are found in limited amounts in environment. Renewable resources such as water (hydro), wind, geothermal, solar and biomass, are regenerated over relatively short periods of time naturally (Figure 1.1) [5].

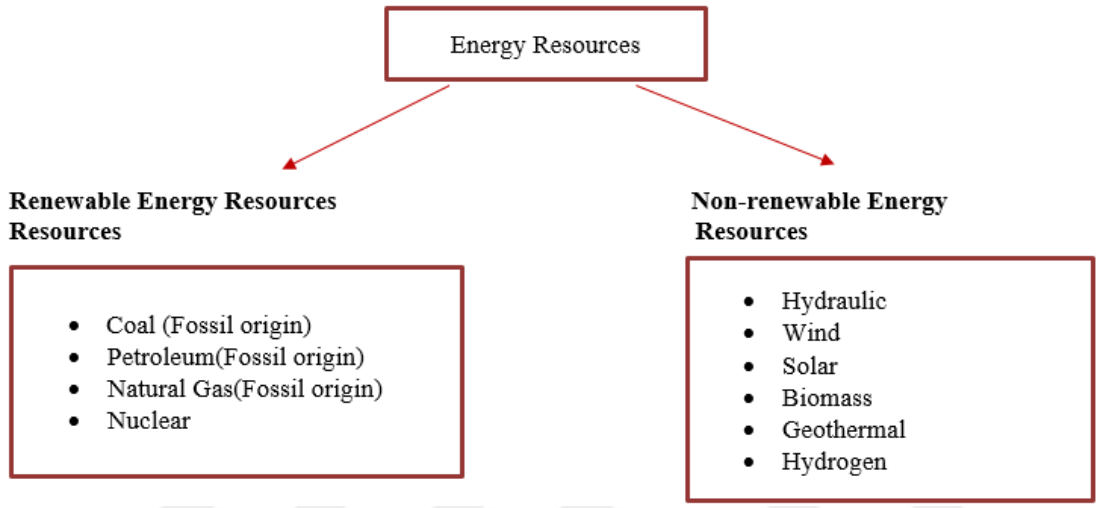
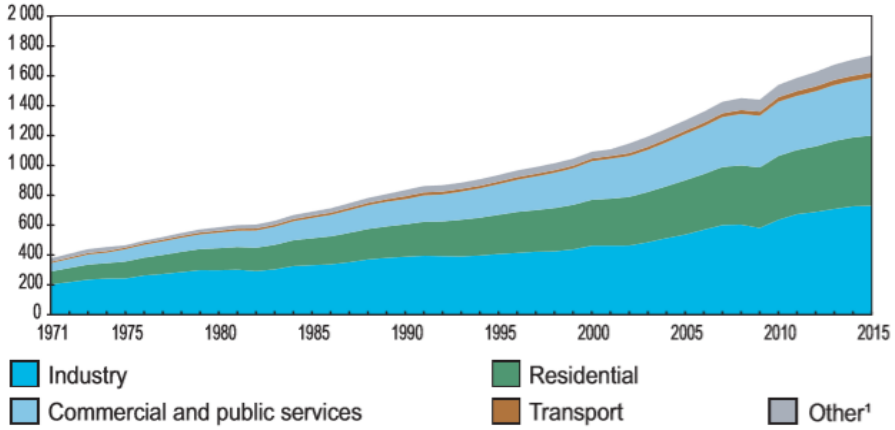


Figure 1.1 Classification of energy resources [5]

According to International Energy Agency (IEA 2017), data's Electricity TFC (Total Final Consumption) from 1971 to 2015 by sector is given in Figure 1.2.

Shares of world electricity consumption between the years 1973 and 2015 are given in Figure 1.3. In 1973, while the share of the industry sector was 53.5 % of total 440 Mtoe energy consumption, the shares of residential sector, transport sector, public and commercial services, and other sectors were 23.0 % , 2.4 % , 15.2% , and 5.9% respectively [6].



[1].*Includes agriculture, fishing and non-specified other.*

Figure 1.2 Electricity TFC from 1971 to 2015 by sector (Mtoe) [6].

When 2015 year is considered, world electricity consumption was 1737 Mtoe. Most of the share was industry sector with 42.0 %, followed by residential with 27.1%. Commercial and public services accounted for 22.2% and while transport sector had a share of 2.1% other sector constituted 6.6% (Figure 1.3) [6].

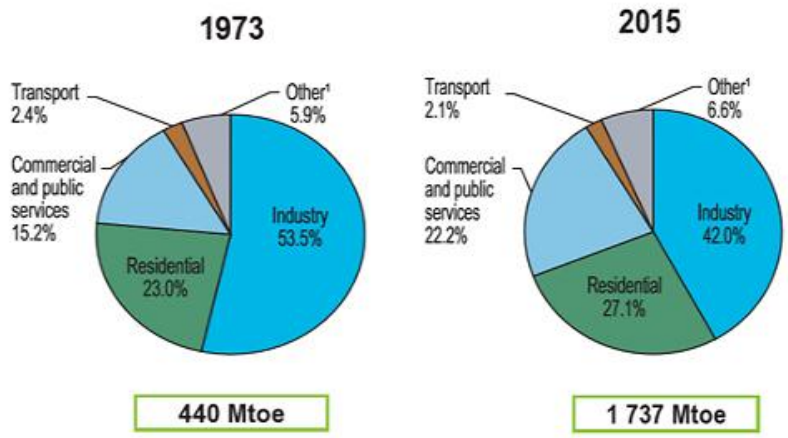


Figure 1.3 The electricity consumption of the world [6]

Utilization of energy generated with high efficiency is of significance to assess potential of alternative and renewable energy sources in addition to the available energy resources.

Particularly in recent years, studies have been focused on clean and environmentally friendly liquid fuels, various chemicals and electrical energy generation from advanced fuels rather than conventional systems from carbonaceous fuels. In this field, gasification

process stands out as an alternative technology that enables the production of clean gas products that can be used in many fields such as internal combustion engine, fuel cell, liquid fuel production. Gasification process has become attractive owing to worldwide increasing environmental sensitivity and restrictions on carbon emissions against global warming.

The conversion of our low-heating value lignite and biomass resources into liquid fuels and various chemicals with gasification technology is an extremely important issue in terms of the use of our local energy resources and ensuring energy security to meet Turkey's growing energy needs.

1.2. Biomass

By comparison with other resources of renewable energy, biomass such as plant, food, animal and urban wastes and forest by-products, is considered the most abundant in nature. Biomass is becoming increasingly important, because fossil fuel resources are limited and affect environment negatively. Biomass is carbon-based renewable resource that does not cause environmental pollution. Additionally, biomass as the fuel it is more difficult to transmit than liquid fuels, and has lower heating value than coal [7]. Biomass energy is defined as any kind of fuel obtained from biofuels and living organisms. Biomass is widely utilized in the world as an energy source obtained by direct processing of animal and plant wastes and provides significant contributions to the world economy [8].

Biomass has three advantageous factors in its use as fuel. Firstly; It is a carbon-neutral renewable resource and can be improved in sustainable bioenergy production. As the second; eco-friendly. It does not conduce to greenhouse gas emissions and reduces the amount of NOx and SOx by replacing fossil fuels. Thirdly; Despite the fluctuation of fossil fuel prices, it has economic potential. Because of the biomass resources distribution all over the world, it creates opportunities such as the development of bio-based economy as well as energy security [9].

Plant biomass is made up of cellulose, lignin and hemicellulose, and slightly amounts of extractives such as lipids and proteins [10].

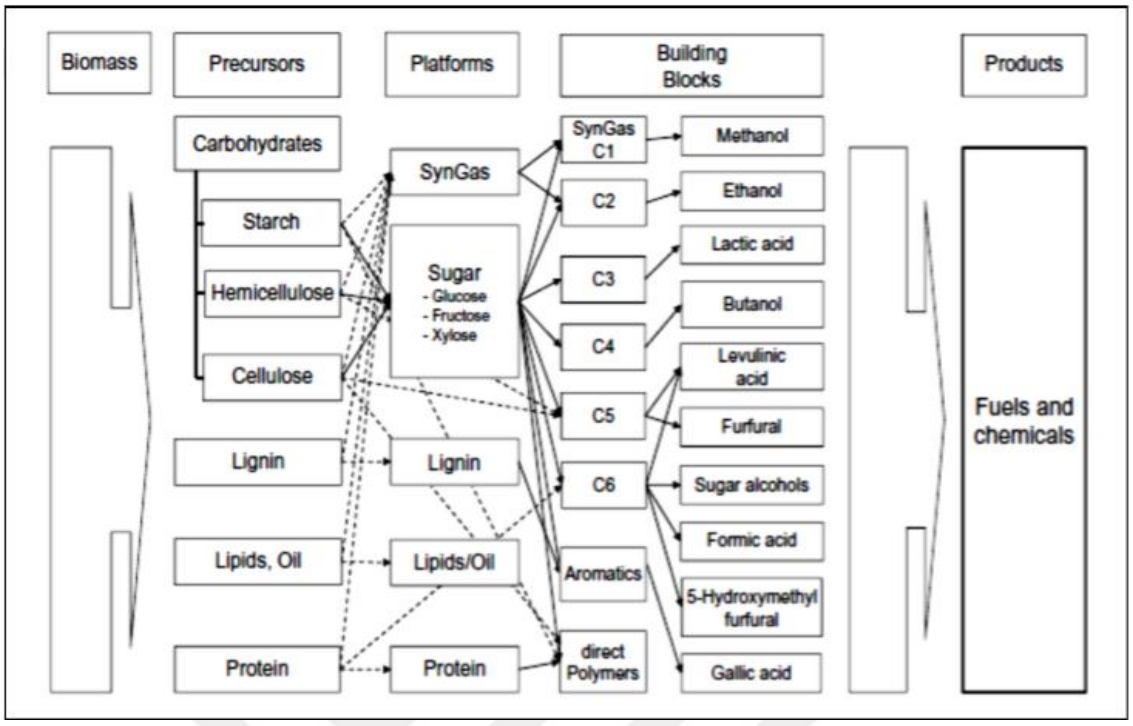


Figure 1.4 Bio-based product flowchart for biomass feedstocks [11]

Plants use solar energy, and carbon dioxide and as outcome of the reaction, oxygen and monosaccharid ((CH_2O) n)are formed (1.1). The sugar polymeric structure, cellulose, is stored in the form of starch or hemicellulose. 75% by weight of most biomass is sugar polymer [12].

$$nCO_2 + nH_2O + \text{light} + \text{chloropyl} \rightarrow (CH_2O)n + nO_2 \quad (1.1)$$

Cellulosic biomass includes three main organic compounds; cellulose, hemicellulose and lignin. Respectively, cellulosic biomass 25-35% hemicellulose, 40-45% cellulose, 15-30% lignin and up to 10% other components [13] . Cereals, potatoes have a starch content of approximately 50% [14].

Cellulose, a biopolymer, is a polysaccharide composed by the binding of D-glucose by β-glyosidic bonds and its molecular formula ($C_6H_{12}O_6$). Cellulose is composed of strong intramolecular and intermolecular hydrogen bonds. Due to its straight chain structure, it has a high degree of crystal structure. It is resistant to enzymes and insoluble in water. On the other hand, it undergoes rapid hydrolysis under subcritical conditions [15]. The breakdown products of cellulose are given in Figure 1.5.

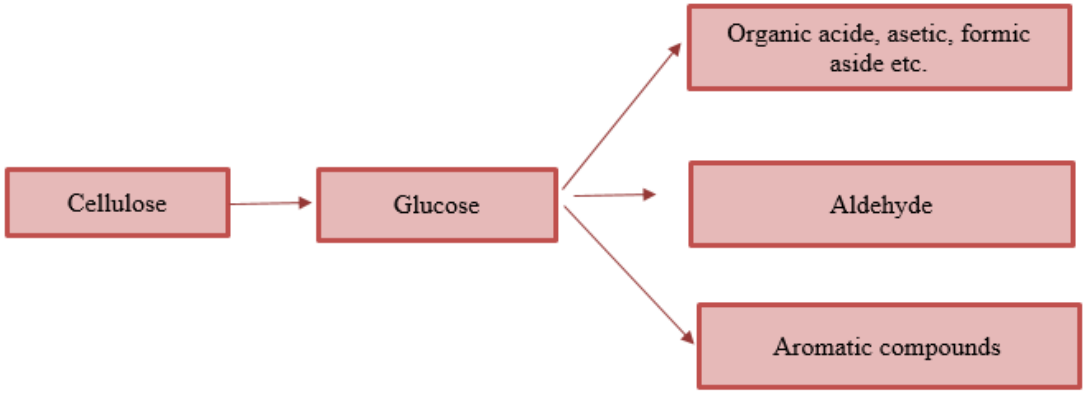


Figure 1.5 The breakdown products of cellulose [15]

Hemicellulose, composed of mixed polysaccharides, is an important carbohydrate fraction of plants, and forms polysaccharide microfibrils by attaching to cellulose with hydrogen bonds. On the contrary cellulose, it consists of side chains. Biomass contains structures called extractives, inorganic components that form water and ash in addition to components like hemicellulose, lignin and cellulose. The extractant is comprise of phenolic compound, aliphatic acid, alcohol, sugar, amine, ether and it is solvable in polar or non-polar solvers [16, 17].

Biomass is an eco-friendly and clean energy source. Even though carbon dioxide is released as biomass is burned, the use of carbon dioxide by green plants during photosynthesis protects the environment from the greenhouse effect. In other words, biomass energy can be said to be piece of the natural carbon cycle. Biomass fuels contain negligible sulphur and do not produce sulphur dioxide, which causes acid rain when burned. By burning biomass, smaller amount of ash is obtained than the ash obtained in consequence of the coal combustion, that can be used as an additive in soil for agricultural purposes [18].

1.3. Coal

Coal is a significant energy resource that widely used in the energy sector throughout the world. Although it was the most utilized feed stock in the production of energy from the Industrial Revolution to the mid twentieth century, it has been replaced by natural gas and petroleum since 1960s. Petroleum (oil) crisis in 1973 with decrease in petroleum

production and the rise in petroleum prices led human beings to renewable natural resources.

Coal is an important resource because it is abundant and widespread throughout the world and is a safe and economical fuel [19]. Coal formation takes place millions of years by accumulation of vegetation in low swamp layers of the earth. Anaerobic bacteria degrade organic materials in oxygen free medium causing the organic material to lose part of its water and under harsh environment. Sediment layer covers it over the years. Coal is a solid, rich in carbon and combustible gases and comprise of inorganic and organic materials [20]. Mainly, coal comprised of carbon, hydrogen, nitrogen, mineral material (inclusive of components of silicon, aluminum, iron and the others). Its formation process varies greatly in terms of geological, petrographic, physical, chemical and thermal properties. Coals are divided into two classes as hard and brown coals depending on calorific value, volatile matter, constant carbon content, coking and caking properties. [19].

There are various compositional distinctions among the coals mined in the world. Different coal types are generally categorized by rank that resides on the conversion degree from the original source. While the gradual conversion process continued, the fixed carbon content and the heating value of the coal increases and the volatile material amount in the coal reduces. The sorting coals method utilized in Canada and the United States has been improved by ASTM and is depend on a range of parameters acquired by different tests. These parameters are given below.

- Volatile matter: The part of a coal sample which is released as a gas when heated without air under the detected conditions is volatile matter. Volatile matter includes volatile organic and inorganic gases like nitrogen, carbon dioxide and sulfur [21].
- Fixed carbon: It is the combustible solid waste which remains after the coal sample is heated and the volatile matter is removed [21]. It consists primarily of carbon containing less hydrogen, nitrogen and sulfur.
- Ash: The inorganic substances left after complete combustion, such as silica, aluminum and potassium.
- Moisture: The water in the coal in case of natural accumulation in the coal. The moisture of a coal sample is measured as the released amount of water when heated under the

projected conditions

- Heating value: When coal (or any other substance) starts to burn totally with oxygen, the energy that is released as heat is called heating value.

Anthracitic coals have the highest fixed carbon components and the lowest volatile content with the highest rank. However, the Lignite coals, have the lowest fixed carbon content and the highest volatile content, thus they are in low rank. The predicted coal percentage of the world for all coal rank is given in Figure 1.6. [22]

In summary, Lignite coal has the lowest heating value while Anthracite coal has the highest heating value.

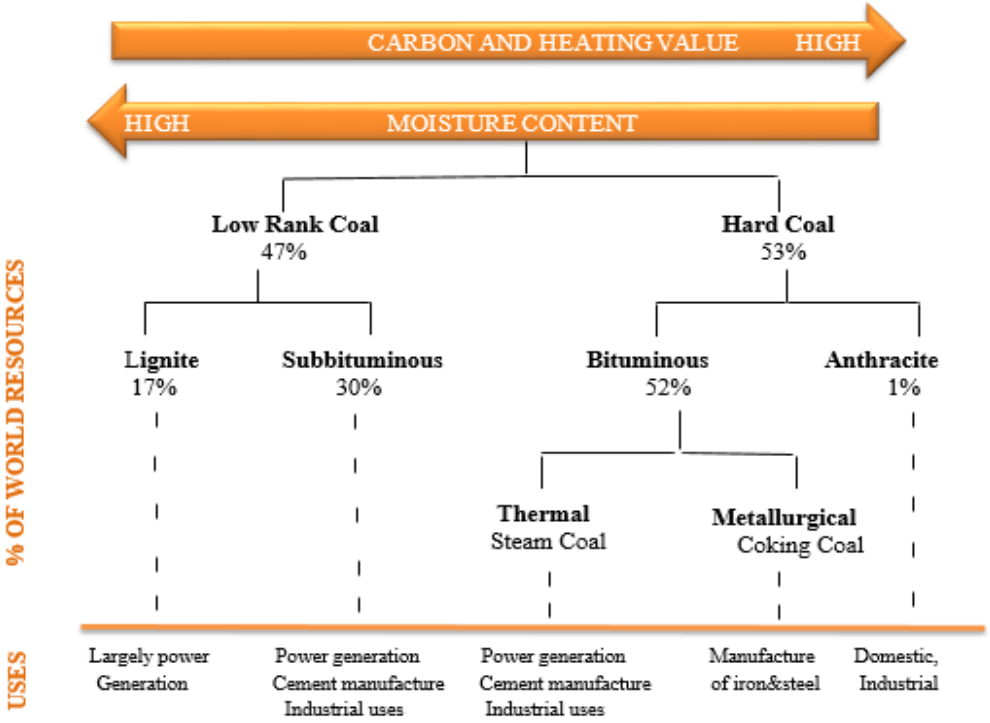


Figure 1.6 The estimated and used coal reserve percentages of the world for each coal rank [22]

Coal is generally used by burning in thermal power plants. As a result of coal burning, some harmful gas emissions such as SOx, NOx and COx are formed [23]. Coal can also be used for domestic, industry, transportation and heating purposes [24]. In 2017, 33% of electricity production in Turkey was covered by coal [25]. According to the BP (2018) report, the world coal reserve is reported to be 1,035 trillion tons. The total coal resources of Turkey is reported to be around 17.25 billion tons [26].

Turkish lignite is generally known to have low heating values. Besides, Turkish lignite is low rank coals because of Turkish lignite's high ash and humidity and low carbon and energy content [27].

Coal is mainly utilized in power plants to produce electricity. It can be also used to generate energy gas, hydrogen, through gasification process since it is not freely found in nature but in the form of compound on the earth crust [28]. Hydrogen has the highest energy content per unit mass; Combustion of 1 kg of hydrogen provides energy equivalent to that of given off by 2,8 kg of oil or 2,1 kg of natural gas. Hydrogen is a very clean fuel. In systems where hydrogen is utilized as fuel, the residual gas is exhausted as just water or water vapor. Hydrogen can be used directly as a fuel in internal combustion engines and for flameless combustion on catalytic surfaces. It is about 33% more efficient than fossil fuels [29].

When hydrogen energy is compared to primary energy sources, it has features such as being portable, abundant in nature, renewable and being able to be stored. It is thought that fossil energy systems will be replaced by hydrogen energy systems [30]. There are many ways to obtain hydrogen. The world's hydrogen demand is met approximately 50% by natural gas, 30% by oil, 18% by coal, 3.9% by water, and 0.1% by other sources [31, 32]. The amount of hydrogen currently produced in the world is approximately 0.1 Gt [33]. To produce hydrogen from coal is by the gasification. Gasification is the method including the conversion of any carbon-containing fuel to a product gas with an available heating value [34]. Carbon-containing fuel in a reactor with high temperature, high pressure and oxygen, the solid fuel undergoes a chemical conversion into gas. [31, 35, 36] This product is called synthesis gas, and it can produce electricity, heat, hydrogen or liquid synthetic fuels [34, 37].

1.4. Utilization of Coal and Biomass

World primary energy production was calculated as 13.790 Mtoe in 2015. Increased by 0.6 % compared to 2014 [38]. In 2015, primary energy production amounts in terms of global resources are shown in Figure 1.7. The major share of this primary energy production is petroleum (4416.26 Mtoe), coal (3871.53 Mtoe) and natural gas (2975.71 Mtoe) from fossil fuels [6].

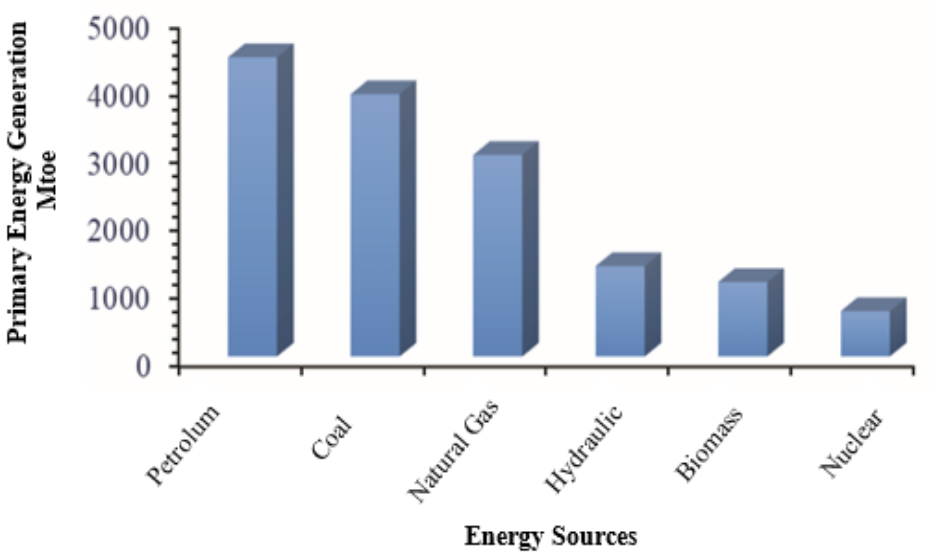


Figure 1.7 2015 source of primary energy production quantities worldwide [6]

Nuclear energy increased by 1.4% and reached 670 Mtoe. Other renewable energy sources such as solar, wind, geothermal and hydraulic have also accelerated compared to previous years [38]. When the energy resources are analyzed, as of the end of 2016, the amount of global energy use is calculated as 13,147 Billion of tonnes of oil. Turkey covers the top 1% of world energy consumption and the amount of 126.9 Mtoe [39]. As of 2016, various energy resources have been used in the world, and they are used in natural gas, petroleum and coal etc. with 85.5%. fossil resources. (Figure 1.8.). According to the information obtained in 2016; petroleum is the highest in energy consumption worldwide with 33.3%. Following petroleum, coal ranked second in energy consumption, 28.1% in natural gas, 24.1% in natural gas, 6.9% in hydraulic, 4.5% in nuclear power, and finally in renewable energy sources 3.2% are consumed (Figure 1.8) [40].

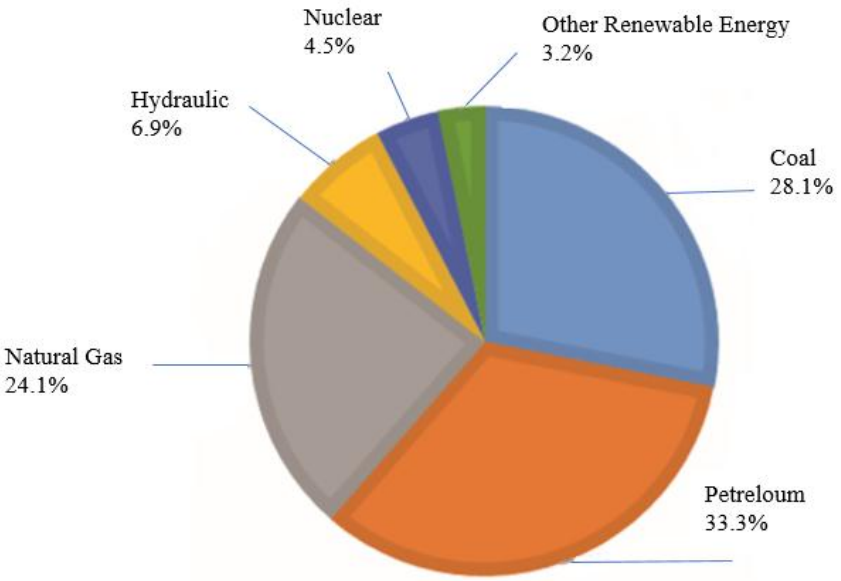


Figure 1.8 The rate of primary energy consumption worldwide by the end of 2016 [40]

Turkey has biomass different agricultural residues. In Table 1.1 is shown the generation of Turkey's fruit and fruit tree residues and their estimated energy value [41].

Table 1.1 The generation of notable agricultural residues in Turkey, (2006)

	Residue	**Heating Value (MJ/kg)**	**Total Heating Value ($x10^5$ GJ)**	**Available Residue(tons)**	**Theoretical Production(tons)**	**Actual Production(tons)**
Apricots	Tree prunning	19.3	13.4	69,571	1,328,846	86,964
Olive	Tree prunning	18.1	39.9	220,627	-	441,254
Pistachio	Tree prunning	19.0	31.9	167,88	-	209,611
Walnut	Tree prunning	19.0	4.8	25,240	-	50,480
Almond	Tree prunning	18.4	4.2	22,800	13,076	28,500
	Shell	19.38	4.6	23,205	44,366	25,784
Hazelnut	Shell	19.3	87.5	453,510	698,499	566,437
	Tree prunning	19.1	332.2	1,742,389	-	2,177,986

As of the end of 2016, it is seen in Table 1.2 that the lignite reserve is 12.712 million tons (Mt) and the hard coal reserve is 1.297 million tons. As of the end of 2016, 1,5 Mt hard coal and and 27 Mt lignite were generated. [42]

Table 1.2 Public coal reserve and production information by the end of 2016

	Institution	**Reserv (million tone)**	**Production(million tone)**
	TKİ	3.646	13,7
	EÜAŞ	8.502	13,3
Lignite	MTA	564	-
	Total	12.712	27.0
Hard Coal	TTK	1.297	1,5

1.5. Gasification

Thermochemical processes are categorized as pyrolysis, gasification and combustion. Various reactor types, working conditions and outcome products are subjects in all thermal processes.

The commercial applications of gasification technologies and the production of fuels and chemicals in this way have a history of over 100 years. With the increase in industrialization and population growth, the increase in energy demand has led to the research for alternative technologies. Therefore, gasification technology has rapidly developed and gained importance as one of the alternative systems where energy can be obtained. Synthesis gas obtained in gasification reactors (syngas) has reached a different dimension in both fuel and chemical production [43].

The most important advantages of gasification are:

- Generation of electricity, production of basic substances used in chemical production and production of liquid fuel,
- Presence of different types of feedstocks such as coal, large molecular oils, petroleum coke, biomass and agricultural waste,
- Removal of pollutants in feedstock and production of clean synthesis gas,
- Converting wastes and low-value materials into valuable products,
- To contribute for the decrease of solid waste amount disposed of in landfills.

Gasification can be defined as the process in which carbonaceous materials are converted into combustible, synthetic gas. CO, CO_2, CH_4 and H_2 in the synthetic gas are of great importance for the process. In general, gasification efficiency depends on the reaction parameters such as, carbon content of the fuel, gasifier type, and the gasifier agents such as oxygen, air, steam, CO_2 or a blend of them at temperatures of about 700°C (1300°F) or higher. As a result of these reactions, the evaluation of synthetic gas and liquid fuels are utilized in both electricity and heat generation [44].

When the carbonaceous substances are heated directly or indirectly in proper gasification conditions, they are pyrolyzed in the first place. During pyrolysis, hydrogen-rich, volatile carbons begin to decompose and release tar, phenols and hydrocarbon gases, as well as a gas product containing a higher proportion of H_2 than the original feed material.
In the gasification process, the feed material becomes saturated with hydrogen. This is explained in two ways.
In the gasification process, the feed material becomes saturated with hydrogen. This is explained in two ways.

- Hydrogen is added directly or indirectly to the system.
- The feed material is pyrolyzed to obtain a product with an H / C ratio greater than the original.

These processes may be carried out separately or simultaneously. If excess hydrogen is added to the system or excess carbon is removed, the final synthetic gas production efficiency of the system is reduced. Catalytic gasification is one example of an indirect hydrogenation process currently under development. In that process, gasification is accelerated with the aid of a catalyst, resulting in hydrogen and carbon monoxide. This process performs at relatively low temperatures and allows the production of CH_4 in the same reactor. Catalyst deactivation and costs are considered as an obstacle to the commercialization of the system in question.

Gasification is carried out in reactors in an environment where solid carbonaceous fuels will come into contact with oxidants (oxygen, air, water vapor or mixtures thereof in various proportions). Many reactions occur in different phases in gasification processes. Figure 1.9 shows the thermal transformation of coal and biomass into the resulting products.

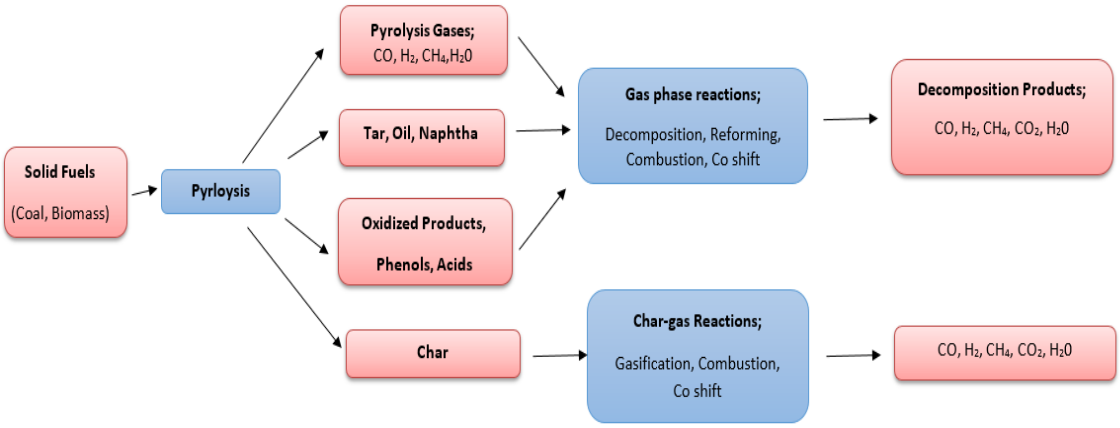


Figure 1.9 Gasification process reactions [34]

In general gasification systems have different physicochemical reactions depending on the temperature. Since the chemical structures of coal and biomass vary, their realization levels vary during the gasification process. These reactions and the temperature range of the reactions can be seen in Table 1.3 [45].

Table 1.3 Stage depending on temperature in gasification

Stage	Temperature
Drying	>150°C
Pyrolysis	150-700°C
Combustion	700-1500°C
Reduction	800-1100°C

Drying

The first process for heating of the solid fuel is drying is. The fuel is heated from ambient to 150 ºC in the atmospheric pressure. Despite it looks like easy, the drying process has three complicated stages [46].

In the first stage, the temperature of the particle increases rapidly, and then water starts to separate first. The drying speed increases significantly in the second stage. The secondly stage is where water is collected on the solid surface and evaporation occurs from the surface. If the solid particle is sufficiently wet, water is transported to the surface in some form as a liquid and forms a thin layer on the surface At this stage, drying takes place at

a rate determined by environmental conditions, regardless of the structure of the solid particle. The drying rate at this stage remains constant if the surface remains wet and the environmental conditions do not change. The concentration difference among the water on the solid surface and the water in the surrounding environment and the temperature discrepancy between the solid surface input the system and the surrounding environment ensure a high rate of drying at this stage. In the third stage, water is separated from the solid by evaporation beneath the surface. When the liquid water layer on the surface is exhausted, the heat transfer causes the water in the pores beneath the surface to evaporate. Evaporated water reaches the surface between the layers of the solid pieces and is separated from the solid pieces. . For this reason, mass and heat transfer resistance in the solid particle remarkably affects the drying rate and drying rate reduces as the thickness of the drying layer increases [47].

Pyrolysis

The pyrolysis phase is a complicated phase in which inorganic and organic compounds are emitted from particle to the nature through diversified reactions by means of heat and mass transfer mechanisms. [47].

There are three kinds of product formation observed in the biomass and coal pyrolysis stage

Formation of light gases: In this phase, gases like CO, H_2, H_2O, CO_2 and CH_4 are removed.

Tar formation: Tar is a black and very heavy, organic and inorganic molecule which is usually emitted from solid particles in gaseous smoke from the liquid part.

Char formation: The solid phase remainder is defined as char. In various types of coals and in almost all biomass, volatile substances constitute an important part of the carbonaceous structure. Particularly in operation, the gases and liquids released during pyrolysis are extremely important because they form a combustible environment around the particle. Pyrolysis is also important in gasification systems as it is a stage that produces product gas.

Combustion

Most of the drying, gasification and pyrolysis reactions are endothermic and should be supported by an external heat source or this heat should be acquired by combustion reactions with an amount of oxygen to be fed in [34].

Because combustion reactions are extremely fast and almost complete reactions, it can be assumed that almost all of the O_2 sent to the gasifier is spent in these reactions. The zone where these reactions occur most in most gasifiers is the zone where O_2 is fed into the system. Therefore, a high temperature profile can be observed in these regions [47]. According to the reactions, carbon and hydrogen are oxidized to produce heat energy. These reactions are exothermic reactions where the temperature is released. They are converted into carbon dioxide and water vapor, respectively. These products decrease the char and pyrolysis products connection. Ash which contains inorganic minerals that do not burn as a result of combustion is also exposed [45, 48].

$$C+O_2 \rightarrow CO_2 + 393{,}77 \text{ kJ/kmol Carbon} \quad (1.2)$$

$$H_2+1/2O_2 \rightarrow H_2O+742 \text{ kJ/kmol Hyrdogen} \quad (1.3)$$

Gasification

Gasification means that the solid fuel is partially or completely converted into gas. The conversion can take place by thermal action or by chemical reactions, or both. When evaluated within this scope, pyrolysis and heterogeneous combustion reactions (between solid and gas) can be considered as gasification. However, in the heat science literature, gasification reactions refer to reactions with gases other than oxygen. Combustion is therefore considered a separate stage. . Gasification reactions are described in two ways with the distinction of homogeneous and heterogeneous reactions. Although gas-gas reactions are homogeneous, they are considered as continuation of heterogeneous reactions.

Gasification is the conversion rate determination stage where the slowest reactions take place. Carbon-containing heterogeneous reactions are Boudouard, Water-gas, and hydrogenation reactions [34].

The Water-gas reaction is a heterogeneous reaction. Carbon monoxide and hydrogen are formed with the same molar ratio as a result of this reaction.

Water-gas reaction; $C + H_2O + 131\ MJ/kmol \leftrightarrow CO + H_2$ (1.4)

The Boudouard reaction is endothermic and the carbon dioxide in the reactor reacts via char to produce CO with this reaction.

The Boudouard reaction; $C + CO_2 + 172\ MJ/\ kmol \leftrightarrow 2CO$ (1.5)

The methanation reaction is a heterogeneous phase.

The methanation ; $C + 2H_2 \leftrightarrow CH_4$ $\Delta H = +75\ MJ/kmol$ (1.6)

Water-gas shift reaction is an exothermic reaction in which carbon monoxide in the reactor reacts with water vapor to form hydrogen and carbon dioxide.

Water-gas shift reaction; $CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H = +42\ MJ/kmol$ (1.7)

Fuel Selection for Gasification Systems

Coal, heavy petroleum products, domestic waste and biomass gasification are used in the process. In order to provide the necessary hydrodynamic conditions when designing gasification systems and to ensure the optimum operation of the system; the particle size, elemental properties and heating value of the coal or biomass to be used; calculations should be made according these properties.

The main considerations in coal selection can be summarized as reactivity of coal, volatile matter ratio, mineral content, mineral composition, moisture content, heating value and ash melting temperature. The selection criteria for coal also apply to biomass. In addition, the other important parameters in terms of biomass density of the biomass, particle size should be considered.

In summary, in the design of gasification systems, some physical and chemical properties of carboneous material should be determined very well [34]. These properties are;

• Thermal value,

• Moisture content,

• Partical size and distribution,

• Compressed density,

• Volatile matter content,

• Constant carbon content,

• Ash content,

• Fuel reactivity,

• Elemental analysis values,

• Pollutant emissions [49].

1.6. Co- gasification Technology

Co-gasification of biomass in combination with other fuels like coal is thought a convenient technology to reduce CO_2 emission [50-56]. The advantages of biomass-coal co-gasification technology are as follows:

• Stabilization of the quality of the feedstock,

• Development of "economic flexibility" of the system,

• Blend of coal and biomass instead of individual use creates a new type of renewable energy source by lowering environmental impact.

• Environmental benefits, such as decreased sulfur and nitrogen emissions by adding biomass to the fuel in the co-gasification.

Biomass is significant, affordable, and eco-friendly. Very few studies include co-gasification of coal with biomass in the world at an industrial scale [57, 58].

Adding a certain amount of biomass to coal provides control of friction and contamination problems leading to substances with high alkali content such as sodium and potassium. Coal and biomass mixtures produce synergistic reactions with high thermal efficiency with lower power output [59].

Co-gasification of coal and biomass can be carried out between the temperature range of 800 °C and 1000 °C (usually higher than 800 ° C) in gasifier using gasification agents like steam, air, nitrogen, oxygen, carbon dioxide, or combining them by direct or indirect heating [60].

The larger molecules of biomass (lignin and cellulose) are separated into lighter molecules, which then turn into lighter molecules such as CO, H_2, CH_4 in combined gasification of biomass and coal. During these transformations, ash, tar, coal and some polluting gases are released. Mass loss in co-gasification was initially determined as; drying of biomass and coal below 125 °C occurring in three stages active pyrolysis between 125 °C and 500

°C and passive pyrolysis above 500 °C [61]. During drying process, the volatiles and most of the moisture are removed. In active pyrolysis stage, while some of the hemicellulose, cellulose and lignin molecules break down, lignin breaks down completely in the passive pyrolysis stage [62]. Above 500 °C, the fixed carbon fraction in coal and biomass causes oxidation and gasification reactions. In particular, water-gas and water-gas exchange reactions between 600 and 700 °C are effective. Above 750 °C, Boudouard reactions are effective.

The experimental study for gasification was realized by Velez et al.[63]. Various mixtures of Colombian coal gasification were investigated experimentally with this study. Rice shells, coffee cups and sawdust were used as biomass. Gasification was conducted in atmospheric ambients by introducing air - water vapor mixture. In the experiments, the synthesis gas composition obtained by changing the air/fuel ratio among 2-3 kg/ kg and steam/fuel ratio among 0.1 - 0.8 kg/kg were examined. The temperature of the steam and air supplied to the system was increased to 350 ºC by preheating. The reactor used was coated with 10 cm thick refractory material via 22 cm inner diameter, and was made of 310 stainless steel at a height of 4 m. The spreader plate used was selected with 142 holes and a hole diameter of 1 mm. A propane-powered burner was used to provide initial ignition in the system.

The syngas obtained was investigated by gas chromatography and the gas composition was analyzed. Since the gas analyzer could not measure methane, the methane amount in the gas obtained from the system could not be found. It was stated that at the end of the experimental study, the gasification of biomass with coal increases the amount of H_2 in the gas mixture obtained, but this effect is small, it is a small effect and it is emphasized that biomass which is a renewable energy source will be beneficial in reducing CO_2 emissions.

1.7. Catalytic Gasification

Catalytic gasification of blend (biomass and coal) is very attractive method because of the higher reaction rate at lower reaction temperature.

Catalyst:

Catalysts are added to the reaction ambient externally, modifying the reaction rate and come out of the reaction without deteriorating its chemical structure. Mainly, three types of catalysis, rely on the state of the material are:

-Heterogeneous,

-Homogeneous,

-Enzyme catalysis.

In heterogeneous catalysis; the reagents, and the catalyst are in various phases In general, the catalyst has solid phase, and the reagents are gas or liquid. Heterogeneous catalysts are significant catalysts used in the chemical industry, particularly in the synthesis of very important basic chemicals type.

In homogeneous catalysis; the reactants are in the same physical state with the catalyst and it is generally liquid. Acid and base catalysis can be given as an example to homogeneous liquid catalysis. In recent years, researchers have worked to prepare a new class of metallic compounds that will serve as homogeneous catalysts. Many of the reactions they catalyze are organic. As homogeneous catalysis occurs mostly under atmospheric conditions, it reduces the cost of production. They can also be designed to be selective for a reaction and cost less than precious metals (Pt, Au, Ru etc.) used in heterogeneous catalysis.

Supported catalysts comprise catalytically active materials, the majority of which are metals. These catalysts may be granular, pelleted, extruded and annular. The supports alone are inert substances which do not have catalytic activity and are a dispersing agent of the active phase. Their effect on catalytic activity depends on the reaction and reaction conditions. They are especially used to improve mechanical strength in weak catalysts. The supports also help the stability of the active structure [64].

Heterogeneous catalysts are classified as synthetic catalysts and natural minerals [65-67]. Synthetic heterogeneous catalysts are categorized transition metal (Ni, Pt and Rh based) and alkaline earth.

Alkali metals belong to the IA group (Li, Na, etc.), are considered to only increase biomass gasification reactions, and are not convenient for direct use as a catalyst for tar reform [68].

CO_2 in the syngas obtained from gasification process can be absorbed by using suitable absorbents, so the H_2 component in the syngas can be enhanced [69]. Calcium oxide (CaO) is an effective and economic material as an absorbent. The addition of CaO to the gasification is an approach used to reduce the amount of CO_2 and tar simultaneously, because CaO is a catalyst that breaks down the tar and absorbs CO_2 gas. The regenerated CaO is then recycled to be used as the CO_2 absorber. It is known that utilization of CaO as a CO_2 absorber in an enhanced high temperature gasification can decrease the quantity of tar in the syngas [70].

1.8. Gasifier Types

Depending on the type of reactor selected, carbon conversion, temperature distributions throughout the reactor, the amount of particles in the product gas will vary, as well as the composition and thermal values of the final products to be directly affected by the reactor type. The reactor types are mainly categorized into three types as fixed bed gasifiers, fluidized bed gasifiers and entrained flow gasifiers [71].

1.8.1. Fixed Bed Gasifier

Fixed bed gasifiers are historically the oldest type of gasification and are appropriate for small and medium-sized plant. It is not preferred in large-scale plants because the content of the synthesized gas exported as the product is unpredictable. Fuel is also typically fed from above and moves downwards under the influence of gravity in the fixed bed gasifier [72]. As the fuel moves downward, it undergoes drying, thermal decomposition and gasification. Fixed bed gasifiers are divided into drying and de-vaporizing, reduction, combustion and ash zone. The required amount of heat for the gasifier is supplied by burning some coal in the combustion zone. Syngas from fixed bed gasifier reactors includes hydrocarbon, water and tar. Solid particles of coal and biomass remain in the gasifier reactor for several hours, while the syngas generated in consequence of gasification is extracted from the system in a few minutes. It is preferred that the particle size to be around 6-50 mm. In addition, the outlet temperature of the synthesis gas varies between 425 °C and 650 °C [34].

The fixed bed types are sorted as updraft, downdraft and crossdraft gasifiers in accordance with the flowing direction of air and gas.

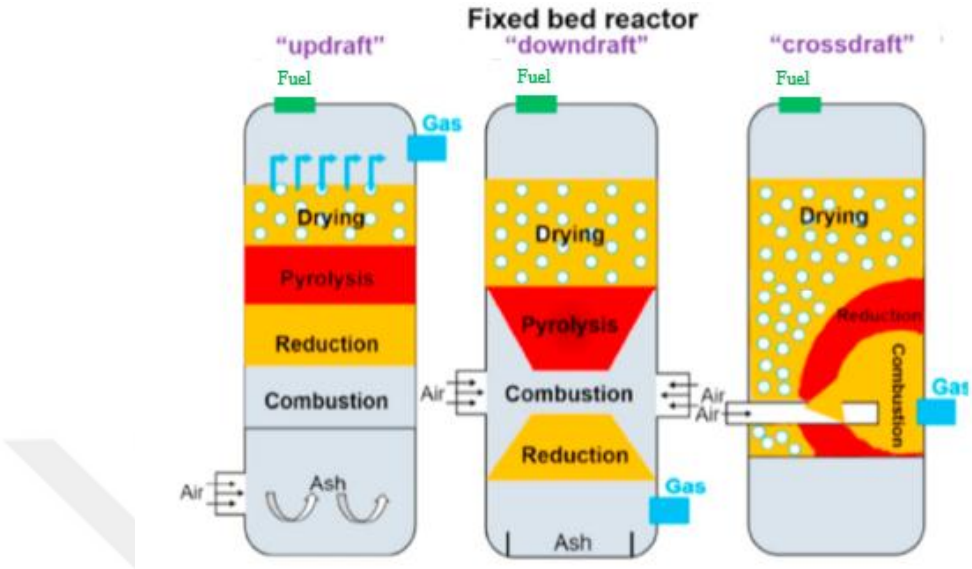


Figure 1.10 Fixed bed gasifier [68]

Updraft Gasifier

Updraft gasifiers have high efficiency as hot gases pass through the fuel column and leave the gasifier at a relatively low temperature. The airflow is provided opposite to the fuel flow and as low as possible of the gas generator. The gas produced is taken from the top of the gasifier. The sensible heat taken from the gas is utilized to and preheat and dry the fuel. Distillation and drying products that occur in the region; water, tar and oil vapors, which do not pass into the oxidation zone. Therefore, if gasification of high volatile fuels is carried out in these gasifiers, the gas produced will contain a high proportion of tar. Many manufacturers use moist air to improve the quality of the gas and keep the temperature below the ash melting point. The most important design parameters are: the method of air loading, the gas outlet situation, the size and type of the grate, the average amount of evaporating water for the introduction of humid air, the interior of the firebox [73].

Downdraft Gasifier

Since the gas produced in the updraft gasifier includes a high percentage of tar, it is difficult to use in internal combustion engines. Downdraft gasifiers have been developed to eliminate this problem. In this type, the air delivered is in the same direction as the fuel,

downwards, and the gas is ejected from the bottom of the gasifier. The basic assessment is as follows: Tar, oils and vapors released in the distillation zone do not have high temperatures. They must also go through the partial combustion zone to pass through the gas outlet. Here, they pass into high temperatures and break into gas. Thus, very low tar remains in the gas mixture. The most important design parameters are; combustion zone design, air delivery, grill design, throat design. A downdraft type gasifier has a narrowed rectangular cross section on the air inlet portion. This is called the throat, which provides a homogeneous thickness of the hot carbon and permits the passage of distillation gases. Therefore, it is an important parameter in design. Downdraft type gasifiers are not appropriate for gasification of fuels with high content of ash and moisture or high slag. If the humidity exceeds 20 %, this fuel will not be suitable for this system. If the fuel ash content is high, then the grill will have to be rotating. The maximum recommended ash content for this gasifier is around 5 %. Moisture in the fuel and air is sufficient for hydrogen production [74].

Crossdraft Gasifier

Crossdraft gasifiers are not preferred much despite their advantages over downdraft and updraft gasifiers. The major disadvantages of this type of gasifier are; gas outlet temperature is high, high gas velocity, CO_2 reduction is weak. Gas output in crossdraft gasifiers is also different from other types. In many cases, unlike other gasifiers, the ash, ignition and reduction zones are not separated by a grid [74].

1.8.2. Fluidized Bed Gasifiers

In fluidized bed gasifiers, the fuel which is forming to the convenient particle size is gasified by fluidizing in the appropriate gasification environment. Such systems are suitable for gasification of biomass and coal particles between 0.5–5 mm. Sand, lime stone or fuel ash can be used as the bed material. If limestone is added, some of the sulphur is retained in the reactor. During gasification of biomass, silica sand is also utilized as inert bed material. The mixture increases homogeneous temperature distribution and high heat transfer throughout the reactor is obtained in such systems when the fluidization rate is exceeded [45].

One of the major factors to be considered when working the reactor is that the bed temperature does not reach the ash melting temperature. Otherwise, the ash may melt and cause slag formation. The resulting slag bed may clog the fluidization. This phenomenon is also referred to as bed tying. For this reason, fluidized bed systems must always be operated below the ash melting temperature. This value is between 800 - 950 ºC in biomass systems and 950 - 1100 ºC in coal gasifiers.

In fluidized-bed systems, it is extremely important for the gasifier to be supplied to the reactor to be homogeneous and that no dead zones occur in the reactor in terms of hydrodynamics of the reactor. Additionally, the diffuser plates prevent solid particles from entering the duct where air, water vapor or oxygen is supplied to the system. For this reason, various types of distributor plates are used in the gasification reactors. Fluidized bed systems are divided into circulating and bubbling fluidized bed system [45].

Circulating Fluidized Bed Gasifier

In circulating fluidized bed (CFB), fuel and bed material are mixed in a hot environment. Pyrolysis, drying, reduction and oxidation reactions occur in different regions of the reactor due to the intensive solid - gas mixture in such systems. The gassing medium gases fed to the reactor are fed to the system via a distributor plate. Therefore, homogeneous mixture is ensuring. We can say that the temperature distribution throughout the reactor is more homogeneous in circulating fluidized bed systems since the bed substance is present throughout the entire reactor. The fluidization rate is in the order of 5-10 m/s which can remove the bed material from the reactor. CFB is given below in Figure 1.11.

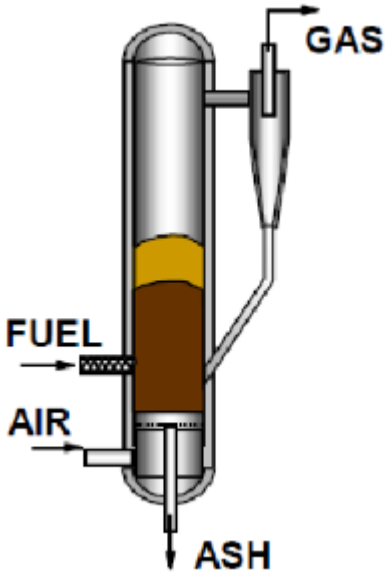


Figure 1.11 Circulating fluidized bed gasifier [75]

Due to high velocity of the gasification medium in the circulating fluidized-bed systems, the reaction time of the fuel fed is shorter than that of the bubbling fluidized-bed systems. This may result in lower reaction efficiency. Thus, the fuel to be fed to the reactor should be smaller in such systems. Furthermore, the bed temperature can be easily controlled and air/fuel ratio can be easily changed compared to fixed bed gasifiers [45].

Bubbling Fluidized Bed Gasifier

In bubbling fluidized bed systems, the rate of gasification medium must be at a certain level in order to begin to fluidize of fuel fed to the bed. The velocity at this point is called the minimum fluidization rate. The fluidization rate in this type of reactor is kept at the order of 2-3 m/s. At higher velocity, the bed expands, causing the bed material to exit the reactor and accumulate in the cyclone. For this reason, high speeds are avoided in bubbling fluidized bed gasifiers [45].

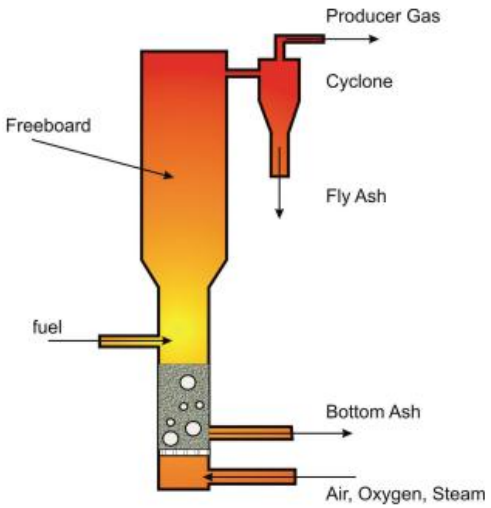


Figure 1.12 Bubbling fluidized bed gasifier [76]

1.8.3. Entrained Flow Gasifier

Entrained flow gasifiers are generally preferred gasifiers in the gasification of coals. In this type of systems, bed temperatures are in the order of 1000 - 1600 ºC, the ash in the bed is removed from the system as molten. Because of the high bed temperatures, almost all of the undesirable tar in the product gas is decomposed and the production of clean synthesis gas without tar can be realized in such gasifiers. Carbon conversion is 99% in such systems. The majority of commercially available entrained flow gasifiers with a successful operation between 20 and 70 bar pressure were established after the 1950s [35].

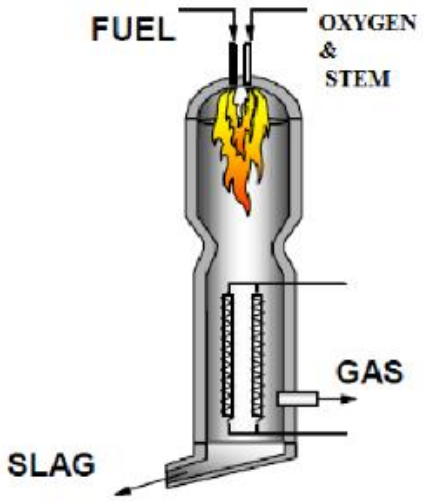


Figure 1.13 Entrained flow gasifier [75]

Entrained flow gasifiers are mostly used in gasification integrated combined cycle power plants for gasification of high energy coals. Coal feeding systems can be found dry coal feed or coal water mixture form [35].

2. MATERIAL AND METHODS

2.1. Sample Characterization

2.1.1. Elemental Analysis

Elemental analysis is made to obtain the relative proportions of the five elements (C, N, S, O, and H) that constitute the organic structure of fuel to a great extent. In elemental analysis of coal, trace elements like F and Cl can also found the elemental analysis [77].

2.1.2. Proximate Analysis

In proximate analysis of the fuel, the moisture, fixed carbon, and volatile matter content with ash are determined.

Proximate analysis was developed for the analysis of charcoal as the method of the American Test and Materials Association (ASTM) D1762-84. It is used in the analysis of many hydrocarbon-based solid fuels, particularly coal [78]. According to the ASTM method, the short analysis requires that the crucible containing the fuel is heated to 750 ° C, cooled and weighed before being used for proximate analysis. In this method the moisture content is calculated as a percentage of the mass loss of samples drying in an inert atmosphere. Volatile compounds of solid fuels are present as a percentage of the mass lost in the range from 105 °C and 950 °C. The ash percentage is the mass remaining as a result of combustion of solid fuel at 750 °C for 6 hours. Short analysis is used in the characterization of the solid fuel composition as a measure of the combustion quality of the solid fuel. When the fixed carbon value of the fuel content is high, the thermal value of the fuel increases; when the ash percentage in the fuel rises, the thermal value of the fuel decreases. Turkish coals generally consist of young coals. Therefore, when the proximate analysis values of Turkish coals are investigated, it is seen that the moisture and ash percentages are high whereas the fixed carbon percentages are low.

2.2. Thermal Analysis

Thermogravimetric Analysis (TGA) shows how mass changes as a function of temperature or time under a certain condition. This method tells about sample composition, and thermal behavior of the sample as it undergoes gasification or any kind of process at specified circumstances. Thermogravimetric analysis is a convenient method for monitoring the thermal and kinetic behavior of solid fuels. It is cheap, fast, and easy technique to determinate composition of solid fuels. In this study, NETZSCH 449 Jupiter F3 was used as thermagravimetry analyzer. (Figure 2.1)

The NETZSCH 449 Jupiter F3 consists of mainly three parts; carrier system and furnace, and balance that measures mass change. Thermagravimetric analyzer NETZSCH 449 Jupiter F3 as a complement to the heater and pressure regulator is used as support equipment. The temperature go up to 1250°C, and can be up to 1600 °C performed studies with normal gas. Protective gas represents the gas to the balance. The gas to the balance should always be inert. The balance should not go into a corrosive substance and the scale should not come into contact with a corrosive substance, in order not to erosion. Purge gases represent the gas leading to the furnace.

Support equipments of TGA device are heat exchanger, pressure regulator, water circulator. The water circulator is used to keep stable the temperature of the balance.

Figure 2.1 TGA device

Heat exchanger is the heating collar and the transfer line. The use of heater exchanger is to prevent condensation of CO_2 or gases. If condensation occurs, the scale of the balance and the system may be corrupted. Purge gas (CO_2) comes from the line and after the pressure is set, it moves to the collar.

The NETZSCH 449 Jupiter F3 device can be used as gasifier in different atmospheres. In this experimental, gasification process was performed under 100 % CO_2 atmosphere.

2.3. Kinetic Analysis

Thermogravimetric methods can examine the kinetics of solid phase degradation reactions. Aim of kinetic analysis is to specify the kinetic parameter effect on the conversion (α).

The method of thermogravimetric analysis includes techniques in which the mass change is recorded as a function of temperature and time if the sample to be examined is heated or cooled in a environment. Depending on the study it can be applied in three different ways [79, 80].

1. "Isothermal thermogravimetry" where the mass of the sample is recorded as a function of time at constant temperature (Model fitting Approach).
2. "Quasi-isothermal thermogravimetry" is the method that the sample is heated until its mass remains constant at each of increasing temperature series (Model Free Approach).
3. "Dynamic thermogravimetry" in which the change in the mass of the material is recorded in an environment where the temperature is changed at a predetermined speed (Nonlinear Regression Analysis Approach).

Different computer programs have been developed to perform kinetic analysis with the data obtained from TG analysis. Malek [81], initiated studies to develop computer programs to operate the kinetic analysis of non-isothermal TG data of solid phase degradation reactions. Perrenot and Widman [82], developed program using the Sestak-Berggran equation and Mettler software language. Elder [83], using Fortran programming language has created an algorithm for the n^{th} order reactions. Malek [81] developed this program for sequential reactions. Mitilky and Sestak[84], generalized the program in question. Flynn [85], determined Arrhenius parameters (E (activation energy) and k0

(frequency factor)) using integral equation. Additionally, Dollimore and colleagues [86] developed another computer program.

In this dissertation, FWO and Friedman method which are model free approaches have been used to kinetic analysis for each gasification experiment.

2.3.1. Model Fitting Approach

2.3.1.1. Coats-Redfern method

Coats-Redfern (1964) kinetic model is based on the integral form of the reaction model. In this integral method [87];

a.A (s) ↔ b.B (s) + c.C (g) (2.1)

In a solid phase degradation reaction according to the equation, the decomposition rate of the substance A is expressed by the kinetic equation (2.2).

$$\frac{d\alpha}{dt} = k.(1-\alpha)^n \quad (2.2)$$

$$f(\alpha) = (1-\alpha)^n \quad (2.3)$$

n= Degree of reaction

(2.2) by taking the integral of the equation linearization, kinetic variables are derived from the equation is calculated. These equations:

1. for n≠1 ;

$$log\left(\frac{1-(1-\alpha)^{1-n}}{(1-n).(T)^2}\right) = log\left(\frac{k_\alpha \mathrm{R}}{bEa}\right) - \left(\frac{Ea}{R\mathrm{T}}\right) \quad (2.4)$$

By selecting the appropriate "n" value, log A ($\log k_\alpha$) and Ea can be calculated from the slope of the line obtained by plotting $log\left(\frac{1-(1-\alpha)^{1-n}}{(1-n).(T)^2}\right)$ versus 1/T.

2. for n=1 ;

$$log\left(-log\frac{(1-a)}{(T)^2}\right) = log\left(\frac{k_\alpha \mathrm{R}}{bEa}\right) - \left(\frac{Ea}{2.303R\mathrm{T}}\right) \quad (2.5)$$

Kinetic variations can be computed from the slope of the line obtained by plotting $log\left(-log\frac{(1-a)}{(T)^2}\right)$ versus 1/T.

2.3.2. Model Free Approach

Generally, the shape of the TG curves will be a function of the reaction kinetics; therefore, it is known that kinetic variables can be calculated from TG curves. Diverse methods developed for this purpose are sorted by Flynn and Wall [88], as follows:

1. "Integral methods" in which weight change with temperature is used directly,
2. "Differential methods" using weight change rate,
3. "Difference differential methods" which take into account the second differences in the rate of weight change,
4. Special methods applicable to initial velocity,
5. Methods using non-linear heating rate.

Solid state decomposition processes may be presented by the following Equation;

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{Ea}{RT}\right) f(\alpha) \quad (2.6)$$

α: degree of conversion

f(α): the reaction model which is a function of conversion

R: Boltzmann gas constant (8.314 J mol^{-1} K^{-1})

k_0: Arrhenius pre-exponential factor

Ea: Activation energy (kJ/mol)

The conversion is expressed as:

$$\alpha = \frac{m_i - m_t}{m_i - m_\infty} \quad (2.7)$$

m_i: Initial mass of sample

m_t: Mass of the sample at time t

m_∞ : Final mass of the sample

For dynamic studies of non-isothermal data a term β as the heating rate (in K/min) is presented the following equation can be obtained[89]:

$$\frac{d\alpha}{dt} = \frac{k_0}{\beta} \exp\left(-\frac{Ea}{RT}\right) f(\alpha) \quad (2.8)$$

Iso-conversional methods can be categorized as integral and differential analysis methods. Differential methods utilize the mainly solid state equation Eq. (2.6), although the integral methods are propped up the integral form of the non-isothermal rate law as the following expression [89],

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{k_0}{\beta} \int_{T_0}^{T} \exp\left(-\frac{Ea}{RT}\right) dT \quad (2.9)$$

where g(α) is the integrated form of the conversion dependence function. If we define x = Ea/RT, Eq. (2.9) can be stated as follows;

$$g(\alpha) = \left(\frac{k_0 E_a}{\beta R}\right) p(x) \quad (2.10)$$

The term p(x) is known as the temperature integral and it has no exact analytical solution [90].

2.3.2.1. Friedman method

The Friedman method is a differential iso-conversional approach that can be given as written below:

$$\ln\left[\beta_i \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = ln[k_\alpha f(\alpha)] - \frac{Ea_\alpha}{RT_\alpha} \quad (2.11)$$

Activation energy (Ea) can be found from the slope of the plotting curve of ln (βi(dα/dT)α,i) versus 1/Tα, at a constant α value. Subscript i is the ordinal number for an experiment performed at a given heating rate [91].

2.3.2.2. The Flynn–Wall–Ozawa (FWO) method

The FWO method developed by Ozawa (Ozawa, 1965) and Flynn-Wall [92] is another integral method for calculating non-isothermal data.

The Flynn–Wall–Ozawa (FWO) technique utilizes the Doyle approximation [93] for the temperature integral:

$$\ln p(x) \cong -5.331 - 1.052x \quad (2.12)$$

Taking logarithm of Eq. (2.9) and combining with Eq. (2.10) gives the FWO expression in Eq. (1.35).

$$ln\beta_i = ln\left(\frac{k_\alpha Ea_\alpha}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{Ea_\alpha}{RT_\alpha} \quad (2.13)$$

Activation energy (E_a) is acquired from a plot of ln(βi), versus 1000/Tα,i, that symbolizes the linear relationship with a given conversion value at different heating rates [94].

2.4. Aspen Modelling

Aspen Plus is a thermodynamic simulation program for physical, chemical and biological applications. Aspen Plus is one of the most preferred programs for overcoming complex situations and simplifying the design of the process. The Aspen Plus program has been and continues to be preferred by many researchers for thermodynamic simulations of solid fuel gasification processes. For example, they modeled the fluidized bed gasification of wood samples by using Aspen Plus. The simulation model is designed to minimize Gibbs free energy and is subdivided into thermodynamic simulations of combustion, pyrolysis, Boudouard reaction and other gasification reactions. The researchers also conducted the sensitivity analysis for the model; examined the effects of air temperature, oxygen factor, gasifier pressure, oxygen content in the air, and superheated steam on gasification performance.

The choice of the reactor generally depends on the size, the type of fuel fed, the composition of the output product, the moisture content, and the vapor/oxygen/air content of the gasifying agent used. Simulation approach is very beneficial because it allows the sensitivity analysis of a process to be performed without operating experimental work. The selection of the appropriate affinity model has helped to attain an optimized process that can decrease costs and the time including experimental studies. The Aspen Plus simulation software used in the modeling of combustion and coal gasification process in combination with integrated biomass and coal gasification to estimate synthesis gas, synthetic natural gas (SNG) and energy generation.

3.1. RESULTS AND DISCUSSION

3.1. Fuel Characterization

Hazelnut husk sample used in the study was supplied from Düzce city of Turkey while Çan Lignite from Çanakkale by Turkish Coal Enterprises Institution. Biomass and coal were pulverized with the shredder "IKA M20 Universal Mill" and sieved to under 250 μm particle size via "Mortar Grinder Retsch RM 200".

Proximate analysis was performed using ASTM standard testing method 5142-04 standards by using "Netzsch 409 PC" TGA device. The results of proximate analysis for biomass and coal can be seen in the Table 3.1.

Table 3.1 The results of proximate analysis for hazelnut husk and Çan Lignite

	Hazelnut Husk (wt %)	**Çan Lignite (wt %)**
M	4,03	3,48
VM	64,30	30,44
FC	22,97	26,14
A	8,70	39,94

M: Moisture, VM: Volatile Matter, FC: Fixed Carbon, A: Ash,

Ultimate analysis was performed using LECO Truspec CHN-S analysis. Table 3.2 demonstrates the ultimate analysis values of coal and biomass.

Table 3.2 The results of elemental analysis for hazelnut husk and Çan Lignite

	Hazelnut Husk (wt %)	**Çan Lignite (wt %)**
C	39,75	32,74
H	5,06	3,00
O	52,30	56,99
N	0,82	0,77
S	2,07	6,50

S: Sulphur N: Nitrogen O: Oxygen H: Hydrogen C: Carbon

3.2.Thermal Analysis

The experiments were performed under 100% CO_2 atmosphere non-isothermally. It was seen that all of CO_2 gasification processes included three subsequent reaction regions which were associated with first pyrolysis, second pyrolysis and gasification stages respectively when the results of TG analyses were investigated.

3.2.1. Experimental Study

All weighted samples (15.0±1.0 mg and < 250μm) was placed in an Al_2O_3 crucible. Samples underwent gasification process in 100% CO_2 atmosphere temperature from 110 ^{0}C up to the 1100 °C in 5, 10 and 15 ^{o}C/min heating rates.

In TGA experimental system; purge CO_2 gas, and argon protective gas flow rates were adjusted to 20 mL/min and 15 ml/min respectively. The reaction starting temperature was 110 °C, and the final temperature was 1100 °C with 5, 10 and 15 ^{o}C/min heating rates.

Correction Experimental Study:

In the beginning of the gasification experiment, the density of the air reduces causing the mass to behave as if it was increasing due to the dominant effect of decrease in the density of the air when the temperature increases.

Correction was required to eliminate any mistake caused mass loss except only by the reactions. In performed experimental studies, the procedure was the same throughout all the heating rates. For all three heating rates correction experiments were performed with empty crucible. (5, 10 and 15 ^{o}C/min).

Correction of TGA measurements are performed by making the experiment with an empty crucible to avoid any interference due to buoyancy effect. The blank curve obtained serves as baseline and subtracted from the sample measurement curve.

The experimental studies were performed in different conditions. The measurements in 100 % CO_2 atmosphere with the conditions are in Table 3.3.

Table 3.3. Experimental studies

Heating Rate	Sample
5 °C/ min	**1.** Hazelnut Husk **2.** Çan Lignite **3.** 50% Çan Lignite + 50% Hazelnut Husk **4.** 40% Hazelnut Husk+ 40% Çan Lignite + 20% CaO
10 °C/ min	**5.** Hazelnut Husk **6.** Çan Lignite **7.** 50% Çan Lignite + 50% Hazelnut Husk **8.** 40% Hazelnut Husk+ 40% Çan Lignite + 20% CaO
15 °C/ min	**9.** Hazelnut Husk **10.** Çan Lignite **11.** 50% Çan Lignite + 50% Hazelnut Husk **12.** 40% Hazelnut Husk+ 40% Çan Lignite + 20% CaO

3.2.2. CO_2 Gasification of Hazelnut Husk

TG and DTG curves of hazelnut husk gasification profile given in Figure 3.1 shows how mass loss varies with increasing temperature from 110 ^oC up to 1100 ^oC at 5 °C/min under CO_2 gasification atmosphere.

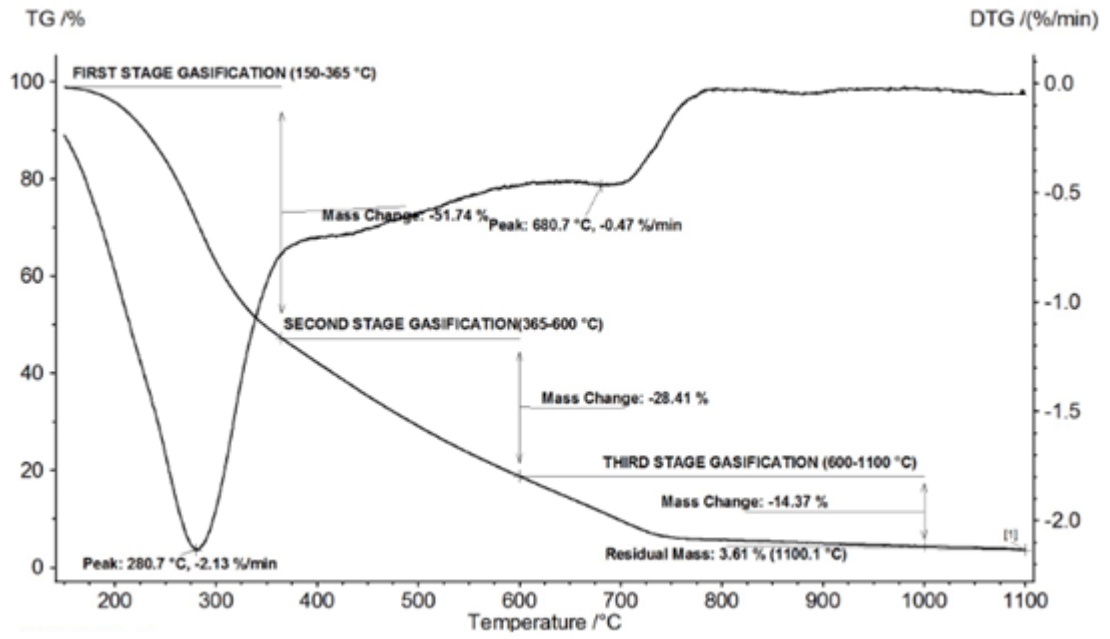


Figure 3.1 TGA and DTG curves of hazelnut husk at 5 °C/min

In DTG curves, the peaks reveal the highest mass change during the process generally arouse from the biomass components decomposition; hemicellulose, lignin and cellulose.

Cellulose and hemicellulose decompose the first since they contain high amount of oxygen. Volatiles from cellulose and hemicellulose are released by the temperature increasing after the moisture evolved. The thermal degradation can be considered as the removal of hemicellulose, cellulose, and lignin parts after moisture release. The dissociation of the cellulose and hemicellulose constituents of hazelnut husk can also be named as the primary pyrolysis zone when the lignin component decompose slowly in the secondary pyrolysis zone.

In Figure 3.1, the gasification reaction took place in 3 steps based on TG and DTG curves. These steps are in the temperature range of 150 °C - 365 °C, 365°C - 600 °C and 600 °C - 1100 °C in the order.

51.74 % of the initial mass loss took place in the first stage mentioned as primary pyrolysis with the maximum loss of 2.13 %/min at 280.7 °C then it was followed by the secondary pyrolysis stage with the mass loss of 28.41 %. In the last stage known as gasification, 14.37 % mass decrease happened with a small peak at 680.7 °C. The maximum loss in that stage was detected as 0.47 %. The residual mass was found to be 3.61 % which can be considered as ash at the end of the gasification. In this last stage most of the fixed carbon separated in the hazelnut husk. Gasification range was observed from 600 ºC to 1100 ºC. The lower temperature peak stands for the hemicellulose component degradation, which happened via a maximum mass loss rate of 2.13 %/min. The degradation proceeds up to a temperature of approximately 380°C. The slow decomposition rate of the lignin ingredient starts continuing up to a temperature of about 600 °C beyond that a small mass change was observed above 380°C [95]. The mass loss of 51.74% indicates that volatile matter is removed from the hazelnut husk. The mass loss of 28.41% indicates that fixed carbon is removed from the hazelnut husk.

3.2.3. CO_2 Gasification of Çan Lignite

TG and DTG curves of Çan lignite gasification profile in Figure 3.2 indicates the mass loss profile against temperature which started from 110 ºC up to 1100 ºC at 5 °C/min under CO_2 gasification atmosphere.

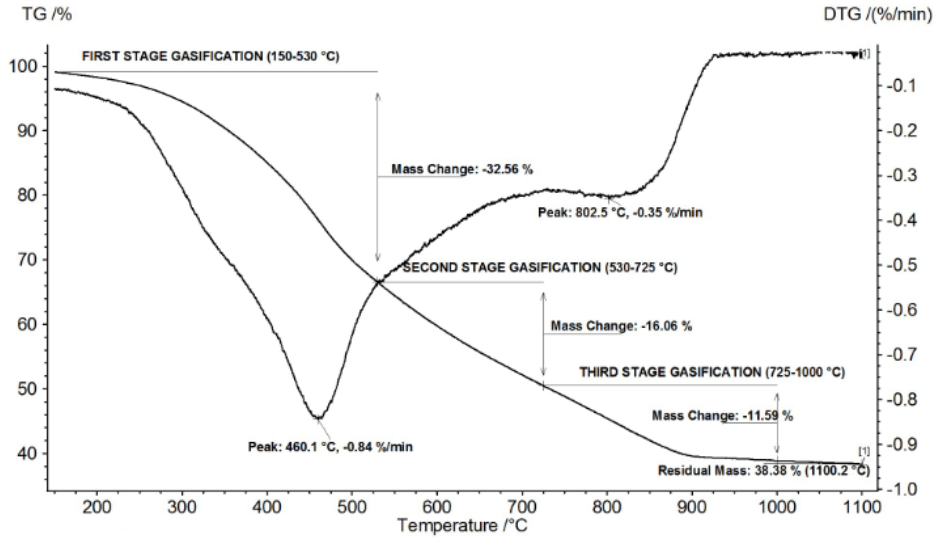


Figure 3.2 TGA and DTG curves of Çan Lignite at 5 °C/min

As shown in Figure 3.2., the zones were stated n the basis of slope changes found in TG curve which were also supported by DTG curve peaks. The TGA curves for Çan lignite under CO_2 gasification atmosphere showed mainly three steps located between 150 °C and 530°C for the first step and between 530 °C and 725 °C for the second step, and the last gasification step between 725 °C and 1000 °C.

The TGA thermogram of Çan lignite under CO_2 atmosphere is in Figure 3.2. The observed thermal changes can be categorized into three temperature ranges. Between the temperature range of 150 °C–530 °C, primary and secondary devolatilization occurs during the thermal process [96]. Over 530 °C, formation and the gasification processes of the char happen. The maximum gasification temperature is found to be ≥ 900°C for Çan Lignite sample.

32.56 % mass loss was detected in the first stage pyrolysis. The mass loss of 32.56 % indicates that volatile matters and other components were removed from Çan lignite. At 460.1 °C, the maximum mass loss (0.84%) of the first pyrolysis fraction occurred. 16.06 % mass loss was in the second pyrolysis stage. It is a gasification zone between 725 °C and 1000 °C. 11.59 % of the mass loss in the last stage refers to the fixed carbon separated in the Çan lignite, while at 802.5 °C, 0.35% to the fixed carbon loss at most. Residual mass can be considered 38.38% as ash content.

3.2.4. Co-Gasification of Çan Lignite and Hazelnut Husk

TG and DTG curves of co-gasification of Çan lignite and hazelnut husk profile given in Figure 3.3 shows how mass loss varies with increasing temperature from 110 ^{o}C up to 1100 ^{o}C at 5 °C/min under CO_2 gasification atmosphere.

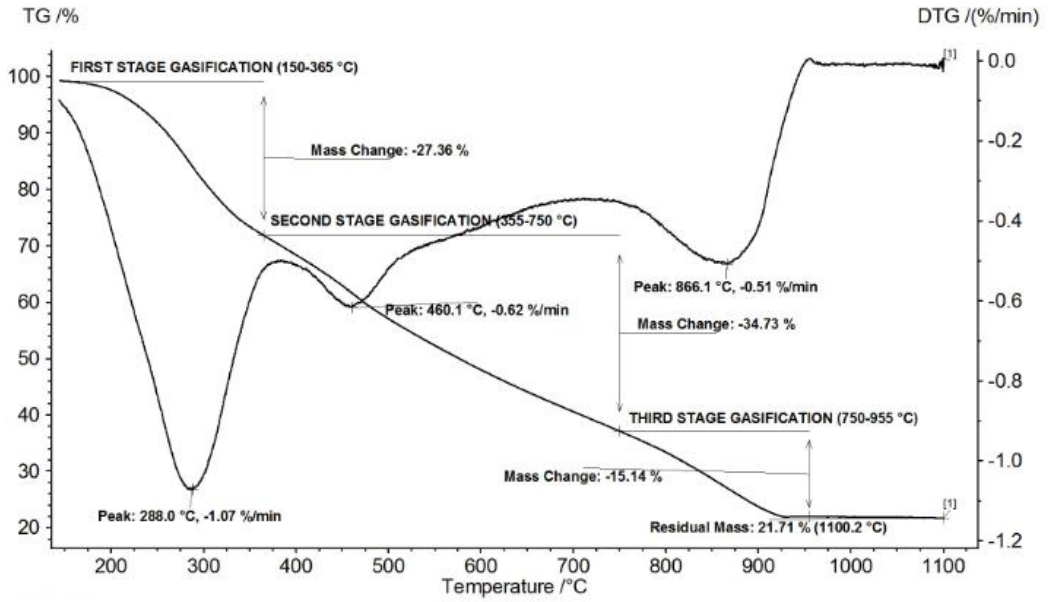


Figure 3.3 TGA and DTG curves of co-gasification hazelnut husk and Çan Lignite at 5 °C/min.

The TGA curves for the blend of Can lignite and hazelnut husk under CO_2 gasification atmosphere showed mainly three steps located between 150 °C and 365°C for the first step, between 365 and 750 °C for the second step. The last step occurred between 750 °C and 955 °C.

There are mainly three stages observed in gasification; dehydration, devolatilization and char oxidation. The first is considered as moisture removal stage. In the second one, most of the mass loss is caused devolatilisation of hemicellulose and cellulose resulting in char formation. In the third stage gasification is favored by char oxidation reactions. All stages are characterized with mass loss rate as can be detected in TG and DTG curves. 27.36 % mass loss was in the primary pyrolysis stage. At 288.0°C, the highest mass loss percentage (1.07%) of the primary pyrolysis occurred and this peak was originated from the removed volatile matters of biomass sample in the blend. 34.73% mass loss was in the secondary pyrolysis stage. At 460.1°C, the highest mass loss (0.62%) of the secondary

pyrolysis occurred and that expresses the removed volatile matters of coal sample in the blend. It is a gasification zone between 750 °C - 955 °C. 15.14% mass loss in that stage refers to the fixed carbon separated in the blend while 0.51 % maximum mass loss at 886.1 °C refers to the removal of biomass and coal fixed carbon at most . Residual mass can be considered 21.71% as ash content.

3.2.5. Catalytic Co-Gasification of the Blend

TG and DTG curves of catalytic co-gasification of Çan lignite and hazelnut husk blend profile given in Figure 3.4 shows how mass loss varies with increasing temperature from 110 °C up to 1100 ºC at 5 °C/min under CO_2 gasification atmosphere.

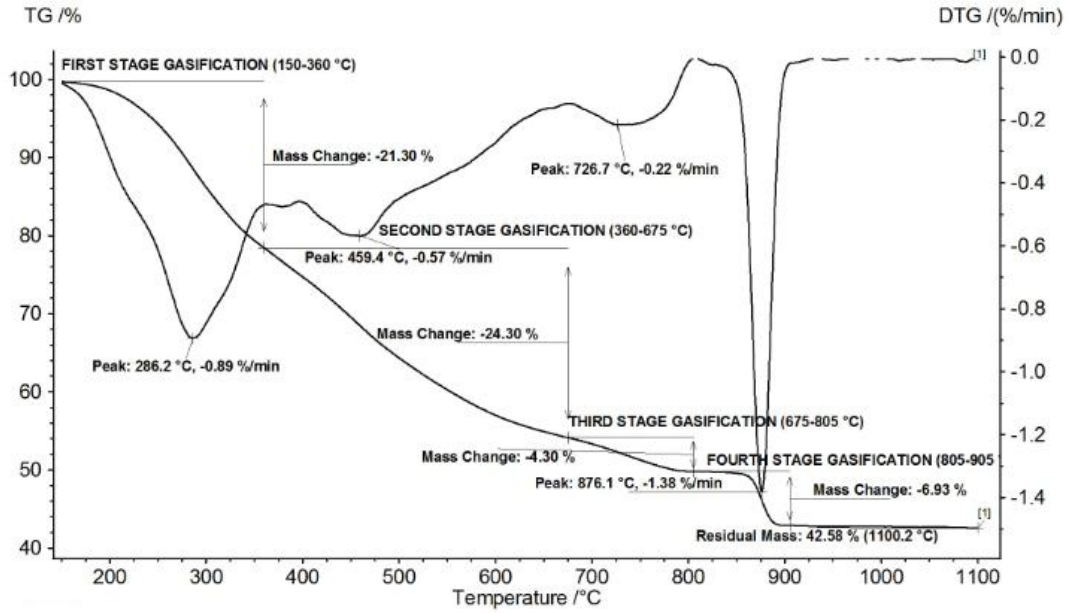


Figure 3.4. TGA and DTG curves of catalytic co-gasification of Çan lignite and hazelnut husk blend at 5 °C/min

The TGA curves for catalytic co-gasification of the blend under CO_2 gasification atmosphere showed mainly four steps located between 150 °C and 360 °C for the first step, 360 °C and 675°C for the second one, and the next between 675 °C and 805 °C. The last step occurred between 805 °C and 905 °C.

Primary pyrolysis stage between the temperature of 150 °C and 360 °C resulted in 21.30 % mass loss with volatile decomposition. At 286.2 °C, the maximum mass loss (0.89%) was detected. In the secondary pyrolysis stage, 24.30 % (360 °C -675 °C) of the mass was lost since the decomposition of lignin and cellulose components of hazelnut husk at

459.4°C, mass loss reached to its maximum rate of 0.57 %. The mass loss of the third stage was 4.30 %. At 726.7 °C, the highest percentage of mass loss (0.22%) of the gasification step where fixed carbon underwent a reaction to produce syngas took place. In the last stage, 6.93 % loss resulted mostly from the decomposition of $CaCO_3$ which could be attributed to the CO_2 released by decomposition of $CaCO_3$. At 876.1 °C it reached to maximum loss with 1.38%. Residual mass of the process can be considered 42.58% as ash content.

3.3. Kinetic Analysis

The mass loss curves examined at different heating rates are thermogravimetrically analyzed to specify the kinetic parameters effect on the conversion (α).

The non-isothermal kinetics of mass loss during the gasification of hazelnut husk, Turkish lignite, blend of hazelnut husk with Turkish lignite and catalytic co-gasification in CO_2 environment between the temperature range of 600 °C - 960 °C were assessed by using FWO method by using the thermokinetic software (Kinetix.3) combined with the instrument.

3.3.1. CO_2 Gasification of Hazelnut Husk

3.3.1.1.Friedman Method

Figure 3.5 shows Friedman iso-conversional curves for CO_2 Gasification of hazelnut husk.

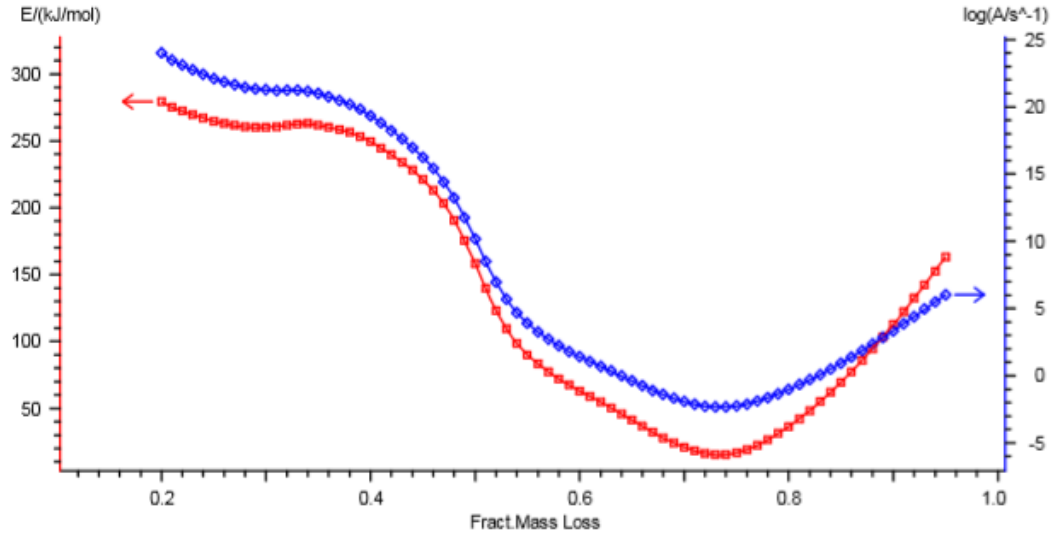


Figure 3.5 The iso-conversional curves of Friedman method for hazelnut husk

The corresponding activation energy versus fractional mass loss values are listed in Table 3.4.

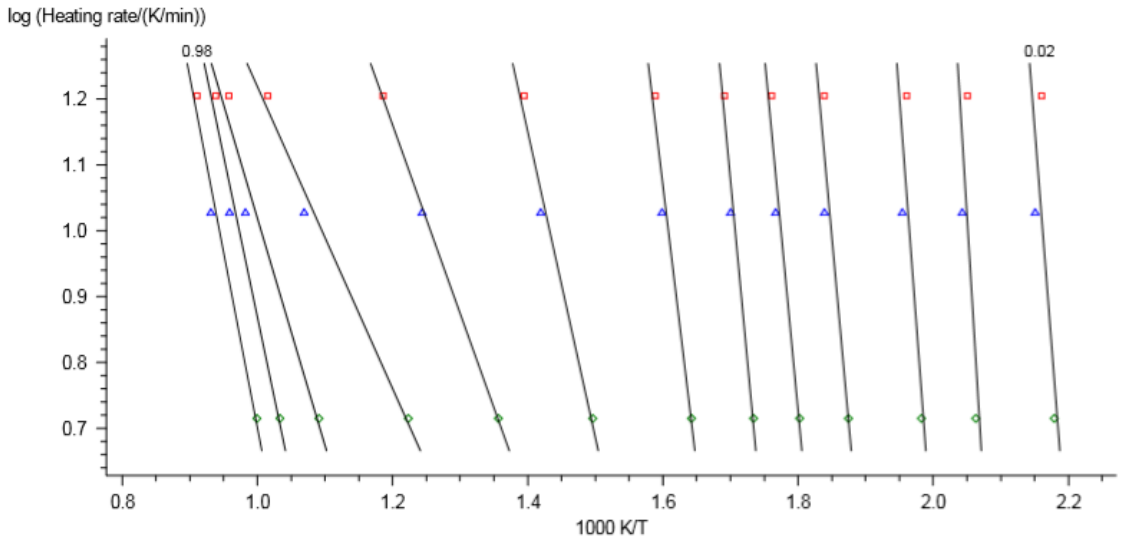
Table 3.4. Friedman Method for hazelnut husk gasification

Fraction Mass loss	Activation Energy(kj/mol)
0.10	334.76
0.20	279.45
0.30	260.24
0.40	249.38
0.50	158.09
0.60	62.96
0.70	20.95
0.80	36.51
0.90	112.67

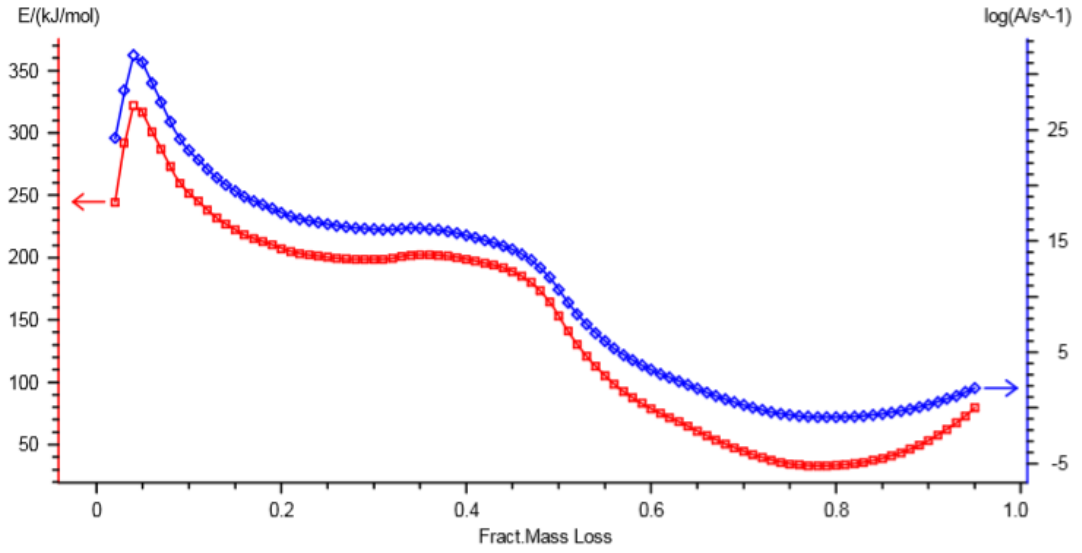
The results of Friedman method for hazelnut husk gasification were studied in three stages. The first stage average activation energy from 0.10 to 0.50 fraction mass loss is about 256.38 kJ/mol, where primary pyrolysis takes place. In the second stage, which is considered secondary pyrolysis, the average activation energy is 41.96 kJ/mol, where the conversion factor is from 0.60 to 0.70. In the final stage, referred as gasification reaction, the average activation energy for conversion factor from 0.80 to 0.90 is about 74.59 kJ/mol.

3.3.1.2.Flynn Wall Ozawa Method

Figure 3.6 shows FWO iso-conversional curves for CO_2 Gasification of hazelnut husk.



(a)



(b)

Figure 3.6 The iso-conversional curves of FWO method for hazelnut husk (a), (b)

The corresponding activation energy versus fractional mass loss values are listed in Table 3.5.

Table 3.5 FWO Method for Hazelnut Husk gasification

Fraction Mass loss	Activation Energy(kj/mol)
0.10	251.72
0.20	207.23
0.30	198.60
0.40	198.72
0.50	153.21
0.60	78.84
0.70	44.56
0.80	33.23
0.90	53.32

The results of FWO method for hazelnut husk gasification were studied in three stages. The corresponding average activation energy in the first primary pyrolysis stage for the conversion factors from 0.10 to 0.50 is about 201.89 kJ/mol. In the second stage, which is considered secondary pyrolysis from 0.60 to 0.70 conversion factor, the average activation energy is 61.70 kJ/mol. In the final stage, where gasification reactions take place, the average activation energy for conversion factor from 0.80 to 0.90 is about 43.28 kJ/mol.

3.3.2. CO_2 Gasification of Çan Lignite

3.3.2.1.Friedman Method

Figure 3.7 shows Friedman iso-conversional curves for CO_2 Gasification of Çan Lignite.

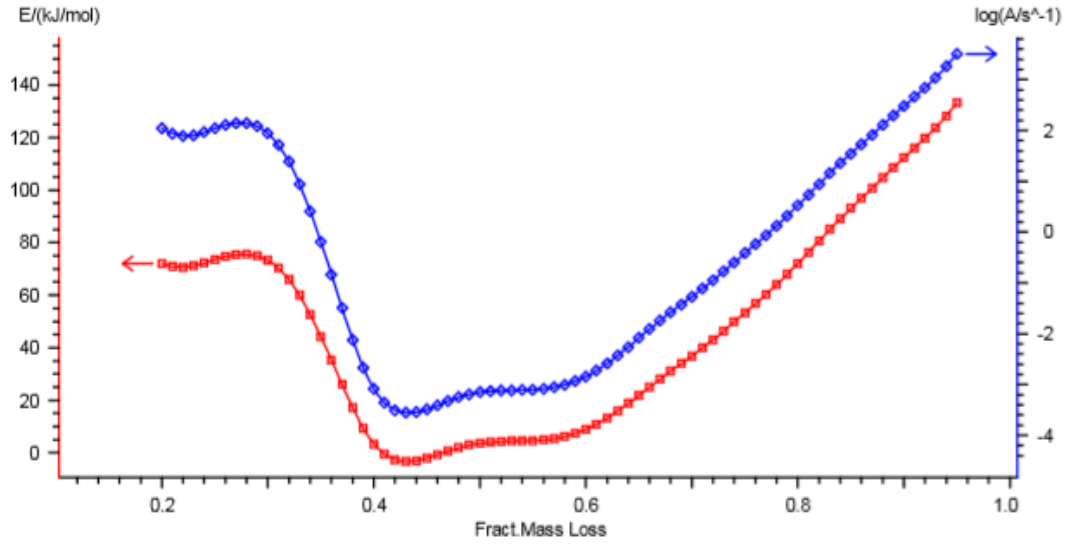


Figure 3.7 The iso-conversional curves of Friedman method for Çan Lignite

Table 3.6 reveals the corresponding activation energy versus fractional mass loss values.

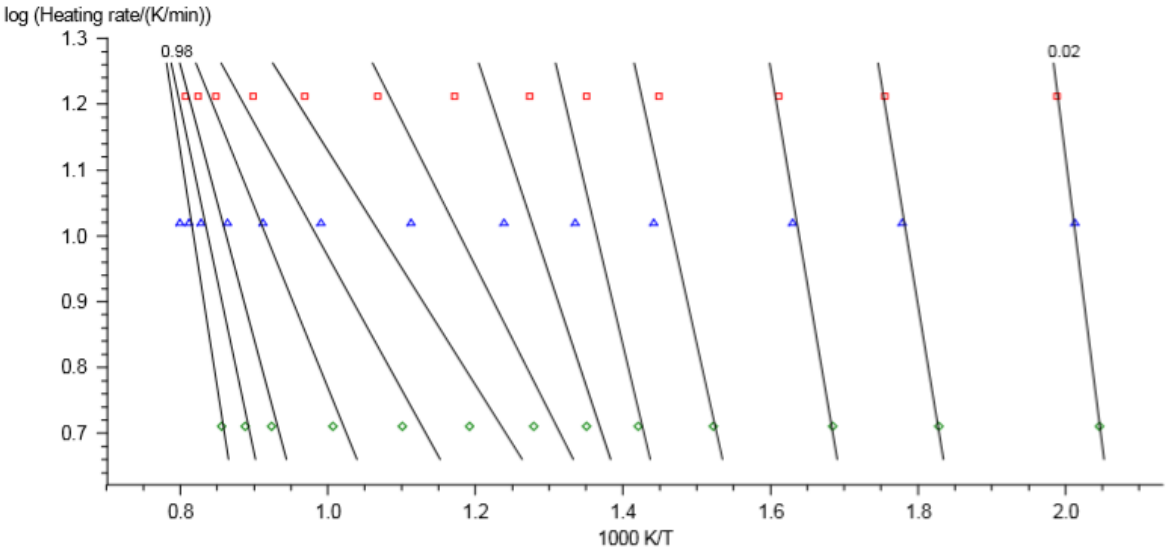
Table 3.6 Friedman Method for Çan Lignite gasification

Fraction Mass loss	Activation Energy(kj/mol)
0.10	116.19
0.20	72.08
0.30	73.35
0.40	3.33
0.50	3.68
0.60	8.93
0.70	36.89
0.80	72.11
0.90	112.33

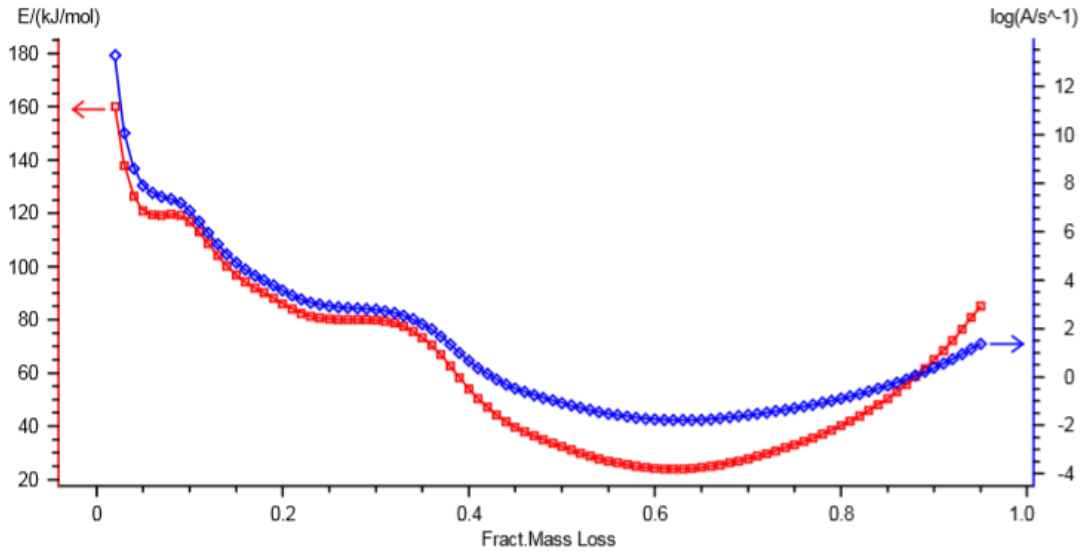
There have been three stages for Çan lignite gasification process with Friedman kinetic method. Average activation energy was computed as 87.20 kJ/mol for conversion factors from 0.10 to 0.30 of the first primary pyrolysis. This value in the second stage, where the conversion factor is from 0.40 to 0.50, average activation energy is 3.51 kJ/mol. In the gasification stage, the average activation energy for conversion factor from 0.60 to 0.90 is about 57.57 kJ/mol.

3.3.2.2.Flynn Wall Ozawa Method

Figure 3.8 shows FWO iso-conversional curves for CO_2 Gasification of Çan Lignite



(a)



(b)

Figure 3.8 The iso-conversional curves of FWO method for Çan Lignite (a), (b)

The corresponding activation energy versus fractional mass loss values are listed in Table 3.7.

Table 3.7. FWO Method for Çan Lignite gasification

Fraction Mass loss	Activation Energy(kj/mol)
0.10	116.80
0.20	86.04
0.30	79.77
0.40	54.01
0.50	32.35
0.60	24.20
0.70	27.80
0.80	40.14
0.90	64.99

The results of FWO method for Çan lignite were studied in three stages. The first stage conversion fraction range is from 0.10 to 0.30, and the average activation energy is about 94.20 kJ/mol, Second stage average activation energy is 43.18 kJ/mol for the conversion factor from 0.40 to 0.50. In the final stage, mass loss fraction starts from 0.60 and the average activation energy is about 39.28 kJ/mol.

3.3.3. CO-Gasification of Çan Lignite and Hazelnut Husk

3.3.3.1.Friedman Method

Figure 3.9 shows Friedman iso-conversional curves for the Co-gasification of Çan Lignite and Hazelnut Husk.

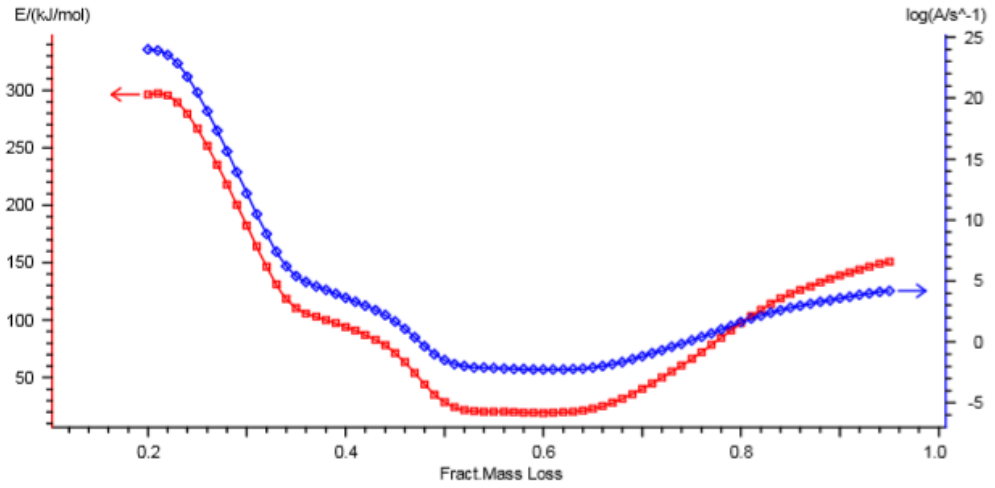


Figure 3.9 The iso-conversional curves of Friedman method for co-gasification of blend

The corresponding activation energy versus fractional mass loss values are listed in Table 3.8.

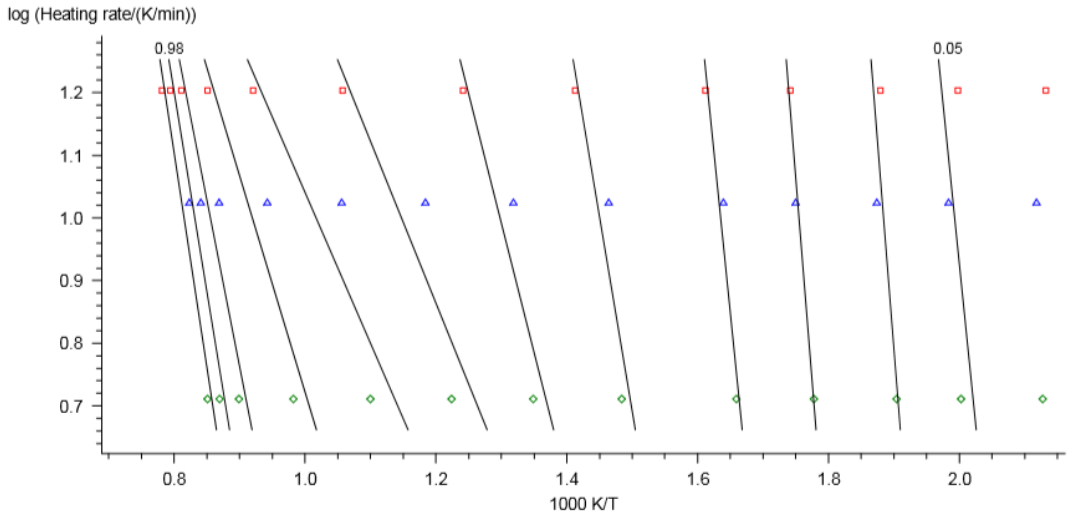
Table 3.8. Friedman Method for co-gasification of blend

Fraction Mass loss	Activation Energy(kj/mol)
0.10	304.92
0.20	296.29
0.30	182.14
0.40	94.14
0.50	28.55
0.60	19.35
0.70	40.16
0.80	97.35
0.90	138.62

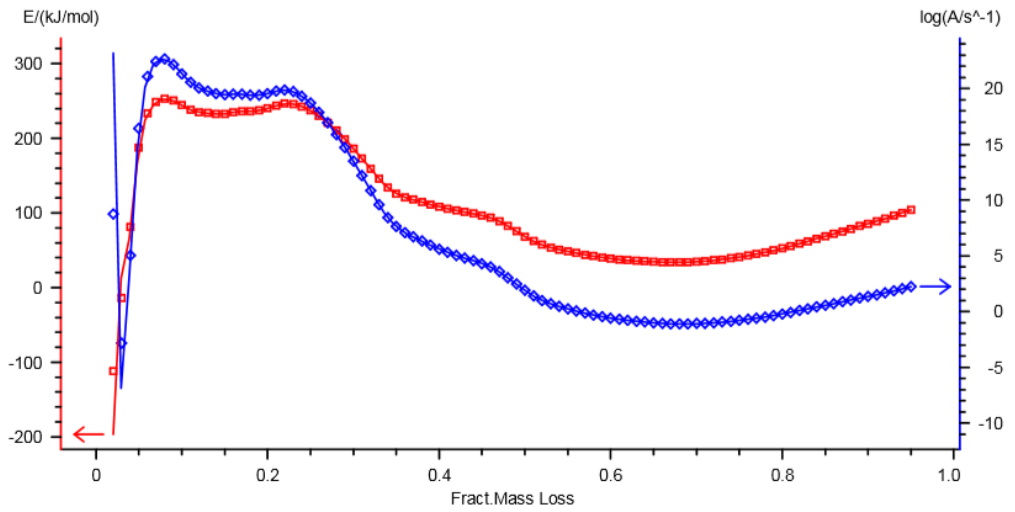
The results of Friedman method for co-gasification of blend have been studied in three stages. The kinetic parameters, the average activation energy for the first stage where mass conversion fraction is from 0.10 to 0.30, are about 261.11 kJ/mol. In the secondary pyrolysis stage, the average activation energy is 47.34 kJ/mol, between the selected conversion range of 0.40 and 0.60. In the final stage, the average activation energy for conversion factor from 0.70 to 0.90 is about 92.04 kJ/mol.

3.3.3.2.Flyn Wall Ozawa Method

Figure 3.10 shows FWO iso-conversional curves for the CO-Gasification of Çan Lignite and Hazelnut Husk.



(a)



(b)

Figure 3.10 The iso-conversional curves of FWO method for co-gasification of blend (a), (b)

The corresponding activation energy versus fractional mass loss values are listed in Table 3.9.

Table 3.9. FWO Method for co-gasification of blend

Fraçction Mass loss	**Activation Energy(kj/mol)**
0.10	244.29
0.20	240.41
0.30	186.39
0.40	108.42
0.50	68.38
0.60	38.80
0.70	34.73
0.80	52.56
0.90	85.78

The results of FWO method for co-gasification of blend have been studied in three stages. The first stage, where primary pyrolysis takes place, the average activation energy for conversion factor from 0.10 to 0.30 is about 223.69 kJ/mol. In the second stage, which is considered secondary pyrolysis, where the conversion factor is from 0.40 to 0.60, the average activation energy is 71.86 kJ/mol. In the final stage, where gasification reactions take place, this value from conversion factor from 0.70 to 0.90 is about 57.79 kJ/mol.

3.3.4. Catalytic CO-Gasification of the Blend

3.3.4.1.Friedman Method

Figure 3.11 shows Friedman iso-conversional curves for the catalytic co-gasification of the blend

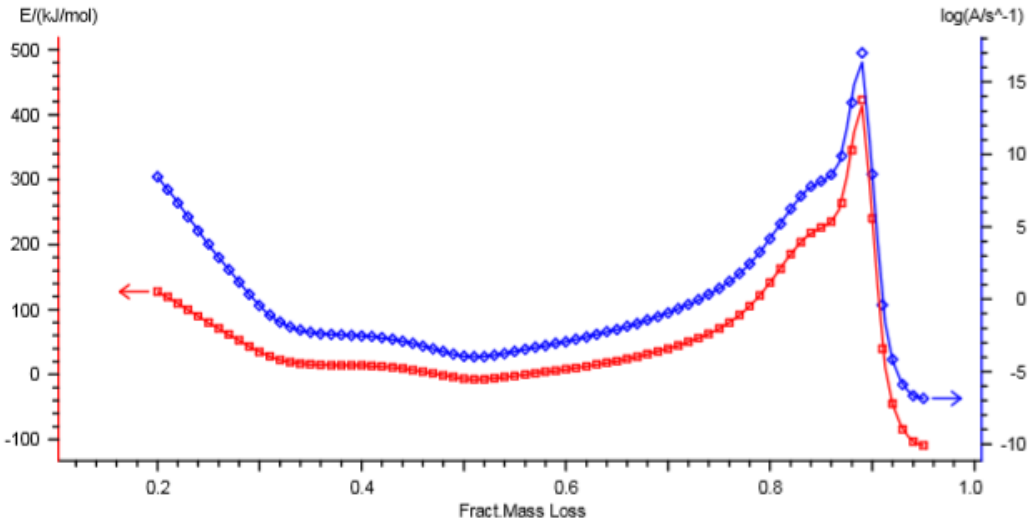


Figure 3.11 The iso-conversional curves of Friedman method for catalytic co-gasification of blend

The corresponding activation energy versus fractional mass loss values are listed in Table 3.10.

Table 3.10 Friedman Method for catalytic co-gasification of blend

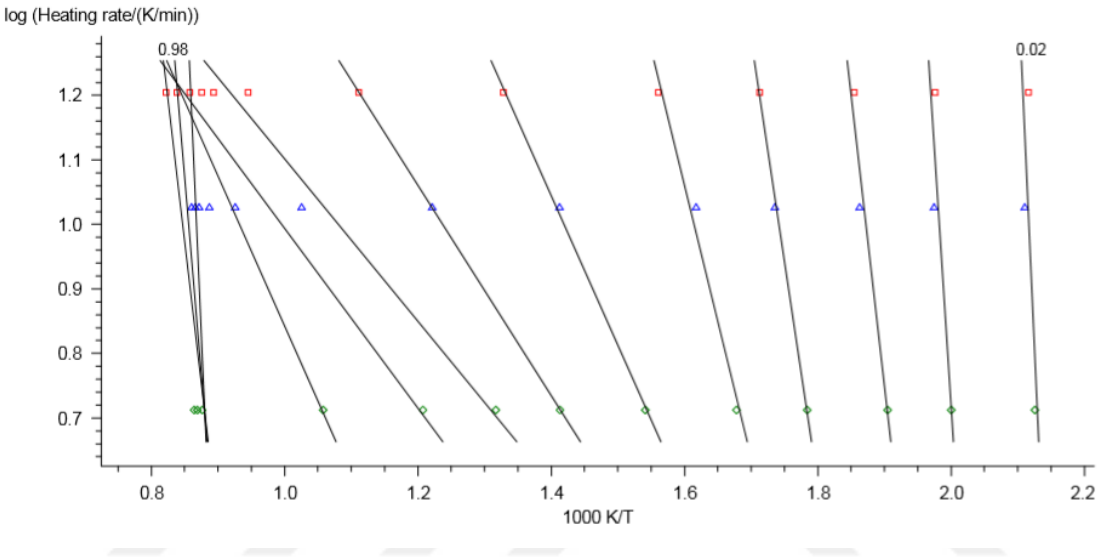
Fraction Mass loss	Activation Energy(kj/mol)
0.10	162.65
0.20	121.18
0.30	70.73
0.40	35.19
0.50	22.23
0.60	15.42
0.70	17.09
0.80	32.00
0.90	413.00

The results of Friedman method for catalytic co-gasification of the blend have been studied in four stages. The first stage, where primary pyrolysis takes place, the average activation energy for conversion factors from 0.10 to 0.20 is about 141.92 kJ/mol, while for the secondary pyrolysis stage, it is 42.71 kJ/mol for the conversion factor from 0.30

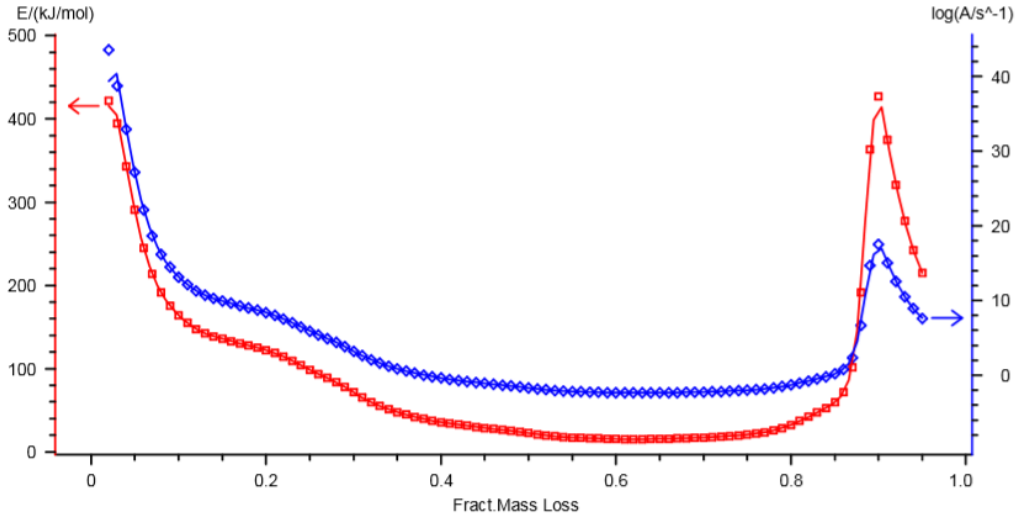
to 0.50. For the third stage, where first of gasification process takes place, 15.42 kJ/mol average activation energy is calculated for the conversion factor of 0.60. In the final gasification stage, the average activation energy for conversion factor from 0.70 to 0.90 is about 154.03 kJ/mol.

3.3.4.2.Flyn Wall Ozawa Method

Figure 3.12 shows FWO iso-conversional curves for the catalytic co-gasification of blend.



(a)



(b)

Figure 3.12 The iso-conversional curves of FWO method for catalytic co-gasification of blend

The corresponding activation energy versus fractional mass loss values are listed in Table 3.11.

Table 3.11 FWO Method for catalytic co-gasification of blend

Fraction Mass loss	Activation Energy(kj/mol)
0.10	164.01
0.20	122.31
0.30	71.52
0.40	35.55
0.50	22.45
0.60	15.50
0.70	17.20
0.80	32.59
0.90	426.86

The results of FWO method for catalytic co-gasification of the blend have been studied in four stages. The first stage, where primary pyrolysis takes place, the average activation energy for conversion factors from 0.10 to 0.20 is about 143.16 kJ/mol, while for the secondary pyrolysis stage, it is 43.17 kJ/mol for the conversion factor from 0.30 to 0.50. For the third stage, where first of gasification process takes place, 15.50 kJ/mol average activation energy value is calculated for the conversion factor of 0.60. In the final gasification stage, the average activation energy for conversion factor from 0.70 to 0.90 is about 158.88 kJ/mol.

3.4. Gasifier Modelling with ASPEN Plus

3.4.1. Assumptions

In this study, CFB gasifier model was operated in Aspen Plus programme. The gasification is depend upon minimizing Gibbs free energy. The process is thought to reach chemical equilibrium from the point of thermodynamics as the Gibbs minimization. The assumptions about the gasification process are given as:

- Steady state and isothermal
- Thermolysis reactions reach the chemical equilibrium quickly.
- Ash doesn't take place in reactions.
- Char includes carbon and ash.
- Heavy hydrocarbons and tar are neglected.
- Feedstock devolatilization products mainly involve CH_4, CO, H_2O, H_2 and CO_2,

3.4.2. Fluidized Bed Gasifier Model Development

The steady-state simulation of the catalytic gasification process in the CFB gasifier was executed in Aspen Plus® V11. Besides, the Soave-Redlich-Kwong (SRK) state equation was chosen with STEAMNBS as the free-water method. The Aspen Plus simulation design for the catalytic gasification process in CFB gasifier is demonstrated in Fig. 3.13.

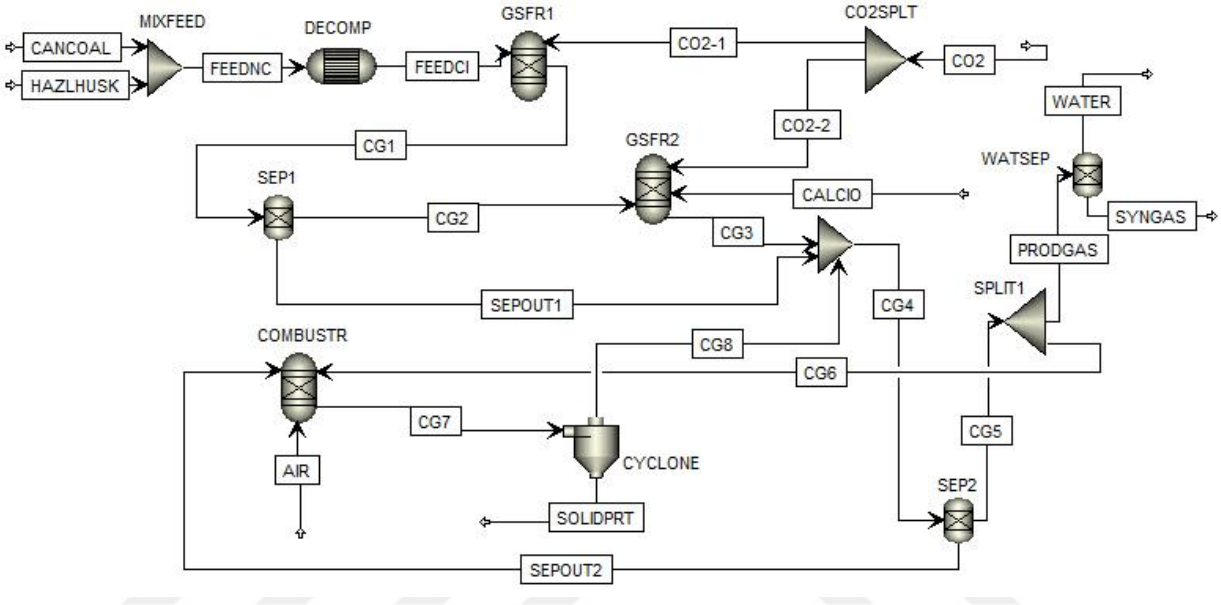


Figure 3.13 The model flowsheet of developed circulating fluidized bed gasifier

The gasification process mainly splitted into three zones that are pyrolysis, gasification, and combustion. The “CANCOAL” and “HAZLHUSK” streams identify the “non-conventional solid” coal and biomass feed. Elemental and proximate analysis for biomass and coal are utilized as feedstock. The mixer was used fort the feding of feedstock streams. The characterized coal and biomass feed enter the yield reactor called "DECOMP" and converts into conventional volatile matters (H2, CO2, CO, H2O, tar and CH4,) and solids (carbon and ash). This reactor may be considered to represent the primary pyrolysis of carbon-based fuel. The fuel gives a reaction by the gasifying agent (CO2) that comes from the separator “CO2SPLT” stream in the “RGibbs” reactors “GSFR1” and “GSFR2“. It can be assumed that secondary pyrolysis occurs in the reactor "GSFR1" after the "DECOMP" reactor. The “GSFR2” block is an “RGibbs” reactor, where the gasification reactions of volatile matters and solids are dominant. However, it should be noted that for “RGibbs” reactors, these reactors determine the products to be released with minimization of Gibbs free energy using the reactants at the specified

temperature and pressure. The reason for saying that they represent pyrolysis or gasification zones is that we can manipulate the composition of the products to be formed by adjusting the temperature of the reactors and the feed rate of gasification agent. Ash and unburned carbon sent to combustion reaction while the “RGibbs” reactor that named as “COMBUSTR”. Solid particles are holded, and the gas is separated in the cyclone. The first reactor products are splitted into a certain rate and prevented from feding into the second reactor in the “SEP1” separator. In the “SEP2” separator, ash and unconverted carbon are separated and fed into the reactor for combustion. The outlet gas, which is substantially free of solid particles in the cyclone, proceeds to the separator called "WATSEP". Table 3.12 gives a brief clarification about the blocks.

Table 3.12 Definition of blocks in the CFB gasifier model

Block Name	**Aspen Plus® ID**	**Description**
DECOMP	RYIELD	Decomposes unconventional solid feedstock into conventional components by using the calculator block
GSFR1 **GSFR2**	RGIBBS	Minimizes the Gibbs free energy and simulates whole gasification reactions
COMBUSTR	RGIBBS	Minimizes the Gibbs free energy and simulates combustion reactions
CO_2SPLT **SPLIT1**	FSPLIT	Dispenses streams homogenously into desired blocks
MIXFEED	MIXER	Combines streams into a single stream
CYCLONE	CYCLONE	Removes solid particles from gas
SEP1	SEP	Separator of the CO (100 %), CO_2 (60 %) and CH_4 (85 %)
SEP2	SEP	Separator of the solid particles (C and Ash)
WATSEP	SEP	Separator of the H_2O (100 %)

3.4.3. Model Validation

3.4.3.1. Validation OF Fluidized Bed Gasifier

Different experimental studies in the literatüre were taken from like input variables, operating conditions and synthesis gas compositions to validate the developed model. A comparison of syngas compositions in experimental studies and simulation results is given in Table 3.13, Table 3.14, Table 3.15 and Table 3.16.

Table 3.13 The comparison of the experimental studies from the new developed model and the literature for coal [97] , [98]

1	Sample	Comp. (%vol.)	Literature	The Developed Model
	Coal Coke	CH_4	1.0	1.8
		H_2	46.0	46.5
		CO	44.0	43.1
		CO_2	4.0	4.1
	Temperature (°C)		800	800
	Pressure (bar)		1.013	1.013
	Fuel Rate (kg/h)		1	1
	Steam Rate (kg/h)		1	1
	Steam Temperature (°C)		152	152
2	Sample	(%dry vol.)	Literature	Model
	Xuzhou Bituminous Coal	CH_4	2.3	2.4
		H_2	10.6	10.0
		CO	10.5	10.7
		CO_2	15.3	14.2
	Temperature (°C)		940	940
	Pressure (MPa)		0.5	0.5
	Steam Rate (kg/h)		3.04	3.04
	Fuel Rate (kg/h)		8	8
	Steam Temperature (°C)		300	300
	Air Rate (kg/h)		25.67	25.67
	Air Temperature (°C)		300	300

Table 3.14 The investigation of the experimental studies from the new developed model and the literature for biomass[99] , [100]

1	Sample	Comp.(%dry vol.)	Literature	The Developed Model
	Hazelnut Shell	CH_4	9.5	9.1
		H_2	28.9	28.9
		CO	21.7	28.4
		CO_2	31.8	32.5
	Temperature (°C)		850	850
	Pressure (bar)		1.013	1.013
	Fuel Rate (kg/h)		122	122
	Steam Rate (kg/h)		48.8	48.8
	Steam Temperature (°C)		-	152
	Oxygen Rate (kg/h)		44	44
2	Sample	Comp. (%dry vol.)	Literature	Model
	Woody Biomass	CH_4	6.0	9.4
		H_2	49.0	49.2
		CO	20.0	19.9
		CO_2	23.0	21.0
	Temperature (°C)		800	800
	Pressure (bar)		1.013	1.013
	Steam Rate (kg/s)		0.45	0.45
	Fuel Rate (kg/s)		1	1
	Steam Temperature (°C)		180	180
	Air Rate (kg/s)		1.84	1.84
	Air Temperature (°C)		280	280

Table 3.15 The investigation of the experimental studies from the new developed model and the literature for biomass & coal mixture [101] , [102]

1	Sample	Comp.(% vol.)	Literature	The Developed Model
	Pine Wood & German Brown Coal	CH_4	5.0	9.0
		H_2	35.0	35.0
		CO	9.0	10.0
		CO_2	18.0	18.0
	Temperature (°C)		800	800
	Pressure (bar)		1.013	1.013
	Steam / Biomass		0.92	0.92
	Biomass : Coal		7 : 3	7 : 3
2	Sample	Comp.(%dry vol.)	Literature	Model
	Tabas Coal & Wood Waste	CH_4	8.4	13.1
		H_2	41.2	40.4
		CO	31.5	31.4
		CO_2	18.8	16.4
	Temperature (°C)		850	850
	Pressure (atm)		20	20
	Steam Rate (kg/h)		6.0	6.0
	Fuel Rate (kg/h)		7.5	7.5
	Coal / Feed		0.5	0.5

Table 3.16 The investigation of the experimental studies from the literature and the new developed model for catalytic gasification [103] [104]

1	Sample	Comp. (% vol.)	Literature	The Developed Model
	Biomass	CH_4	9.1	9.0
		H_2	48.1	48.9
		CO	24.5	23.2
		CO_2	18.3	17.3
	Temperature (°C)		700	700
	Pressure (bar)		0.1	0.1
	Steam / Biomass		0.5	0.5
	Biomass : Coal		0.5	0.5
2	Sample	Comp. (%dry vol.)	Literature	Model
	Sawdust	CH_4	2.5	2.3
		H_2	11.5	11.3
		CO	14.8	14.3
		CO_2	17.5	10.0
	Temperature (°C)		800	800
	Pressure (atm)		-	1
	ER		0.3	0.3
	Steam / Fuel		0.5	0.5

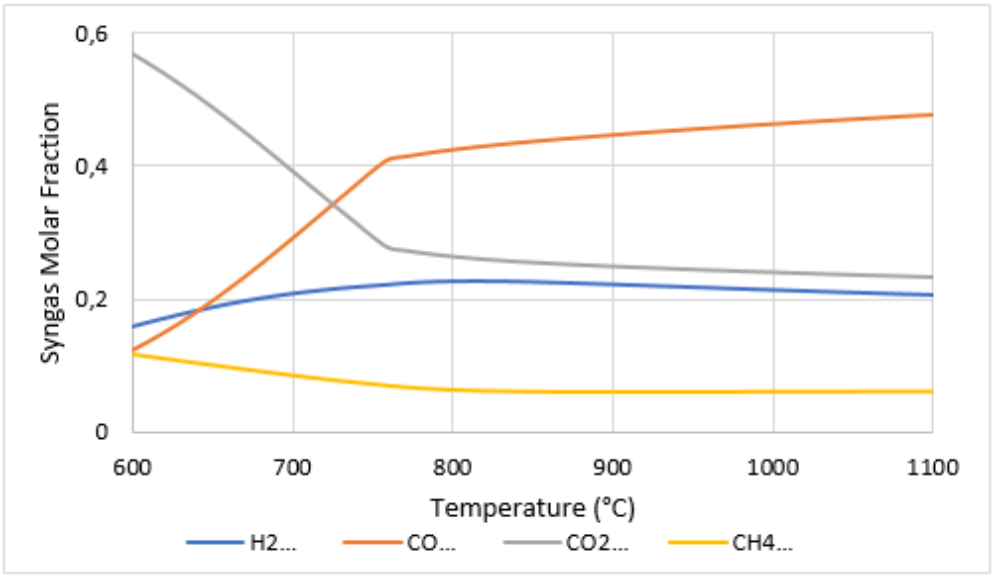
The results for the model effectively show resemblance with the studies from literature as can be seen in tables. The Gibbs reactors used in the simulation program assume that reactions happen fast and reach chemical equilibrium conditions, whereas, in experimental studies, conversion rates of reactions vary depending on the residence time. Therefore, CH_4 may be various in some experiments since the reaction times are not enough for reaching equilibrium conditions in experimental works. The model results are acceptable to apply in fluidized bed gasification processes.

3.4.4. Parametric Study

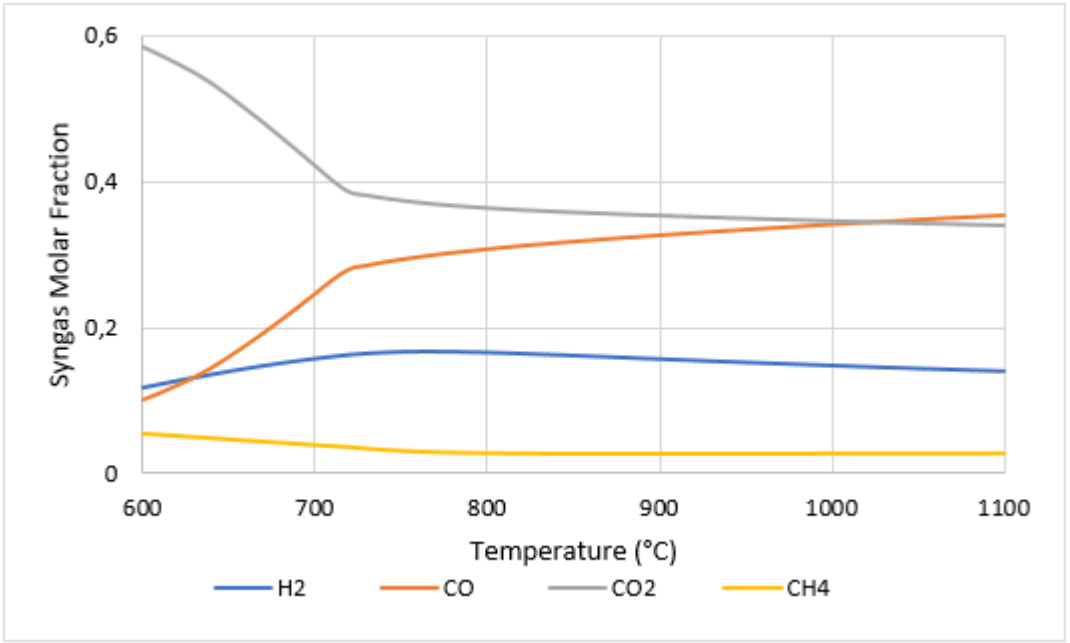
The gasifier pressure and temperature effects as well as the influence of CO_2/fuel ratio on the syngas composition have been researched by parametric studies to evaluate the gasification characteristic properties of hazelnut husk and Çan lignite in the CFB gasifier. Çan lignite and hazelnut husk and were given individually to the gasifier as feedstock and optimal conditions were assigned for each of them. Then, the fuels (50% hazelnut husk, 50% Çan lignite) were fed at the same time for co-gasification and lastly the same processes were done again with CaO catalysis.

3.4.4.1. Effect of Gasifier Temperature on Syngas Composition

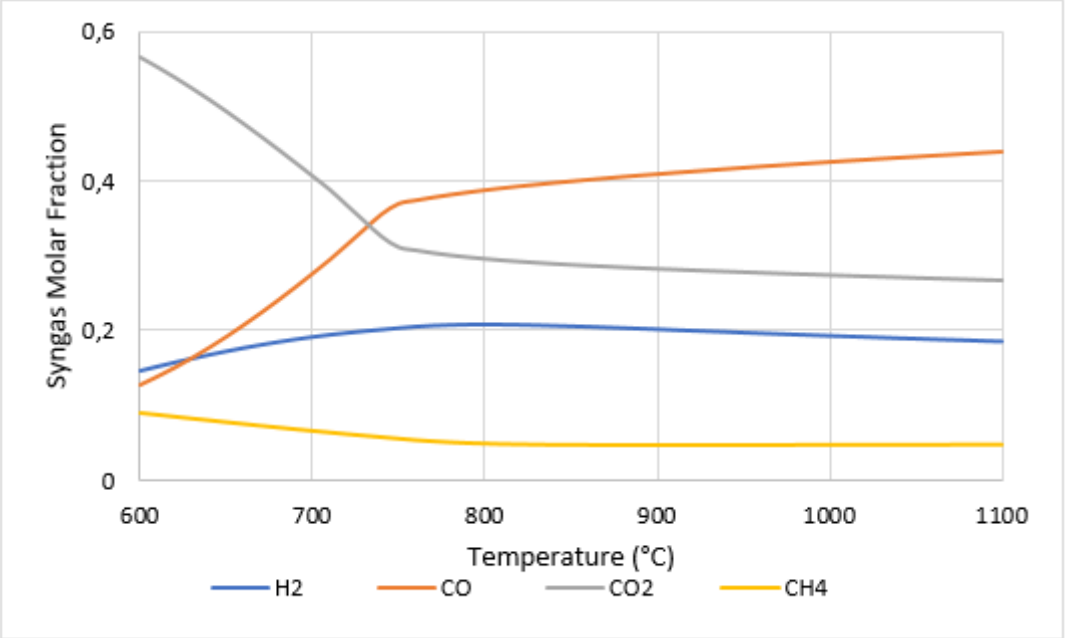
The gasifier temperature influence on the syngas composition for hazelnut husk, Çan lignite and its blend are shown in Figure 3.14. The temperature of gasifier is between 600 °C - 1100 °C, the CO_2 / fuel ratios are 0.65 for hazelnut husk, 0.25 for Çan lignite and 0.45 for their blend and the gasifier pressure is 3 bars.



(a)



(b)



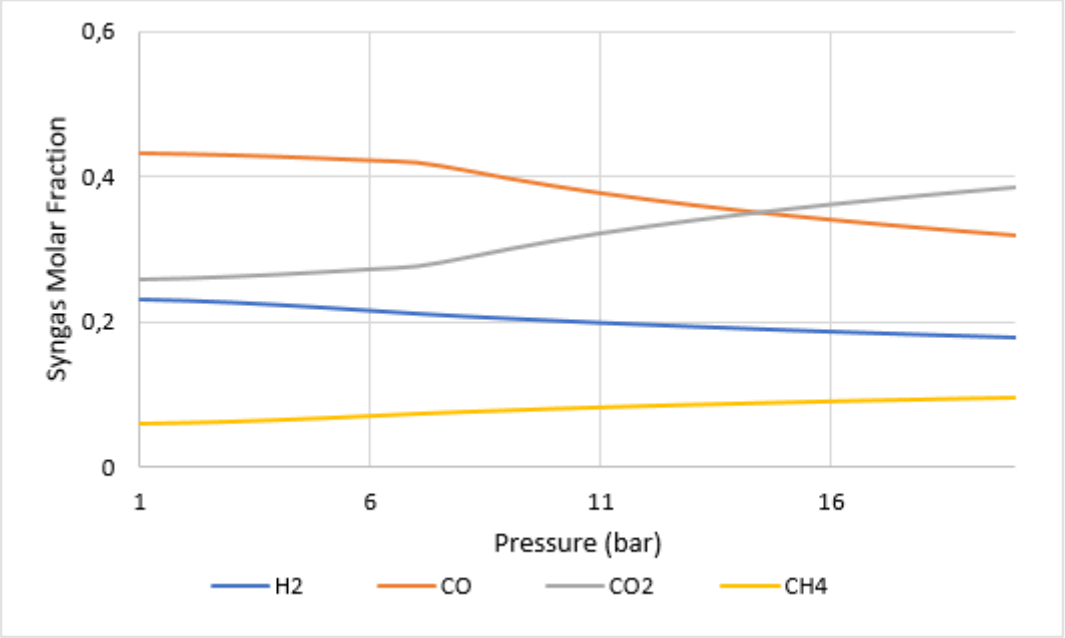
(c)

Figure 3.14 The effect of gasifier temperature on syngas composition; (a) hazelnut husk (b) Çan Lignite (c) hazelnut husk & Çan Lignite Blend

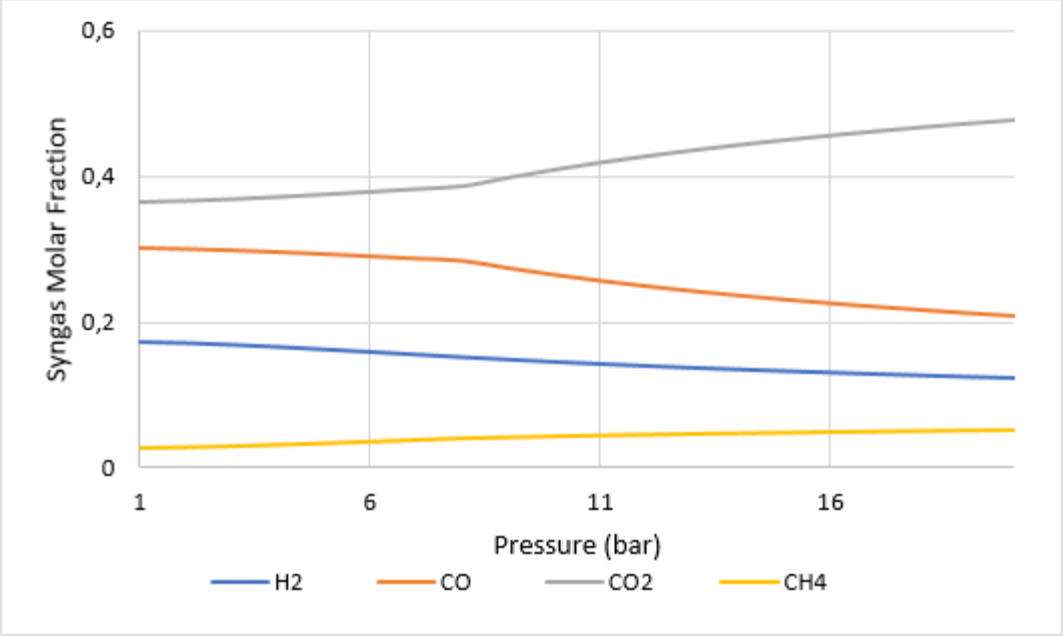
One of the behaviors clearly seen in the Figure 3.14 is that when the gasifier temperature enhances, the CO composition rises, and the CO_2 composition reduces. This can be explained by the driving forward of the Boudouard reaction. However, when the gasifier temperature reaches at a certain point syngas composition change rate by temperature decreases. These temperatures were 760 °C for hazelnut husk, 720 °C for Çan lignite and 750 °C for the blend.

3.4.4.2. Effect of Gasifier Pressure on Syngas Composition

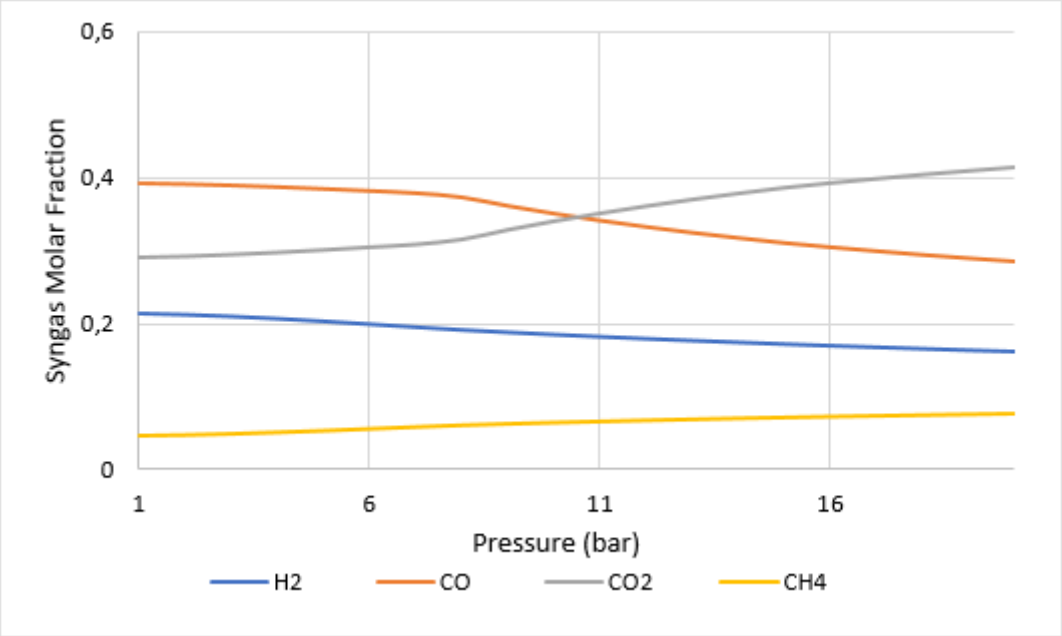
The pressure of the gasifier has major effect on the syngas composition change. The pressure was changed from 1 bar to 20 bar to analyze the gasifier pressure effect on the syngas composition. The temperature in the gasifier is constant at 760 °C for hazelnut husk and 720 °C for Çan lignite and 750 °C for the blend. The gasifier pressure effect on the syngas composition can be seen in Figure 3.15.


0,6
0,4
0,2
0
Syngas Molar Fraction
1
6
11
16
Pressure (bar)
H2
CO
CO2
CH4

(a)


0,6
0,4
0,2
0
Syngas Molar Fraction
1
6
11
16
Pressure (bar)
H2
CO
CO2
CH4

(b)



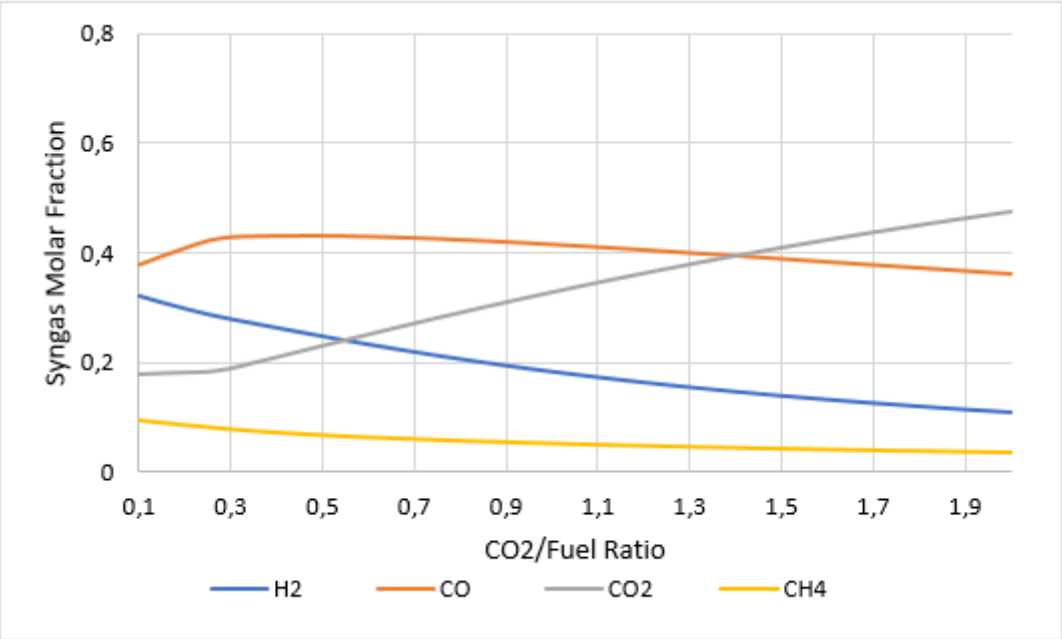
(c)

Figure 3.15 Gasifier pressure influence on syngas composition a) hazelnut husk (b) Çan Lignite (c) hazelnut husk & Çan Lignite blend

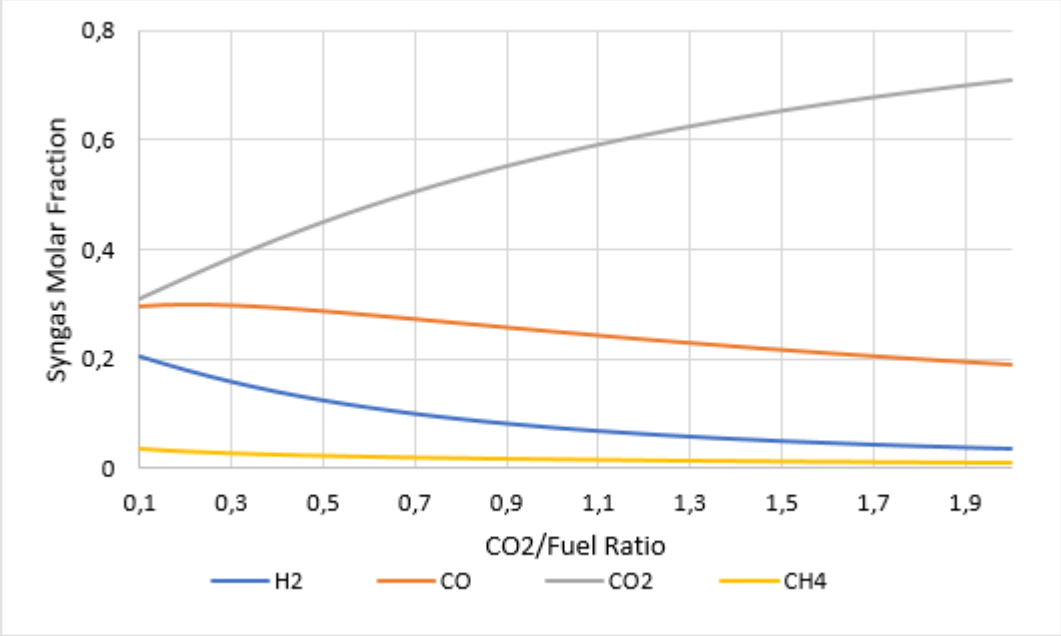
When a dynamic equilibrium is varied with a disturbing factor in accordance with the Le Chatelier principle, the system goes to the direction for minimizing this effect. The gasifier pressure changes the reactions direction and changes the syngas composition, because gasification reactions are also equilibrium reactions. When the gasifier pressure increasing, the amounts of H_2 and CO gases reduces and the amounts of CO_2 and CH_4 gases rises. The decrease in H_2 gas concentration and the increase in CH_4 gas concentration is based on the methane formation reactions, and the reduction in CO gas composition and enhancement in CO_2 composition can be clarified by Boudouard reaction. Only CH_4 composition improves the valuable chemicals at high pressure, thus the system pressure is needed to be setted with this factor is considered.

3.4.4.3. Effect of CO_2/Fuel Ratio on Syngas Composition

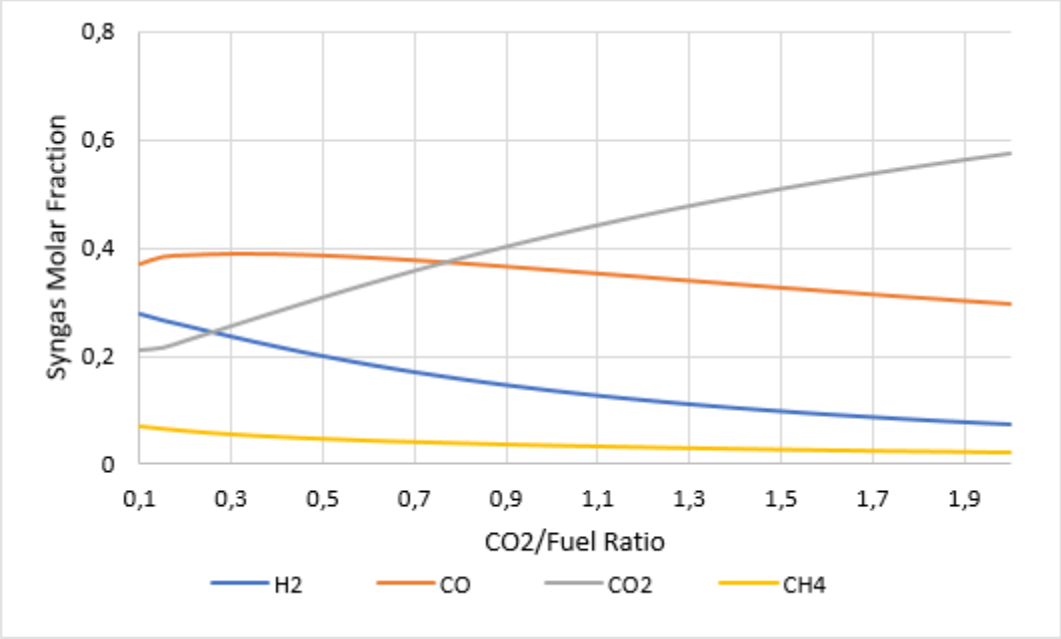
The determination of the CO_2/fuel ratio is significant to obtain CO efficiently in the last of the gasification process. The influence of CO_2/fuel ratio on syngas composition can be seen in Figure 3.16. The ratio ranges from 0.1 to 2 and the pressure of the gasifier is constant at 3 bars and the temperature of the gasifier is constant at 760 °C for hazelnut husk, 720 °C for Çan lignite and 750 °C the blend.


0,8
0,6
0,4
0,2
0
Syngas Molar Fraction
0,1
0,3
0,5
0,7
0,9
1,1
1,3
1,5
1,7
1,9
CO2/Fuel Ratio
H2
CO
CO2
CH4

(a)


0,8
0,6
0,4
0,2
0
Syngas Molar Fraction
0,1
0,3
0,5
0,7
0,9
1,1
1,3
1,5
1,7
1,9
CO2/Fuel Ratio
H2
CO
CO2
CH4

(b)



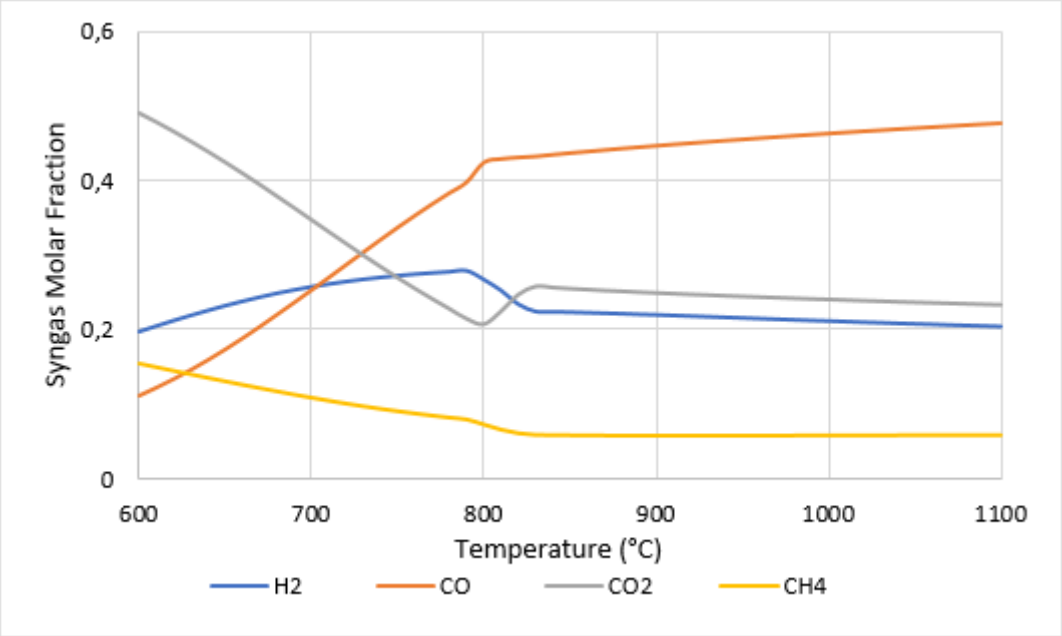
(c)

Figure 3.16. The effect of CO_2/fuel ratio on syngas composition; (a) hazelnut husk (b) Çan Lignite (c) hazelnut husk & Çan Lignite blend

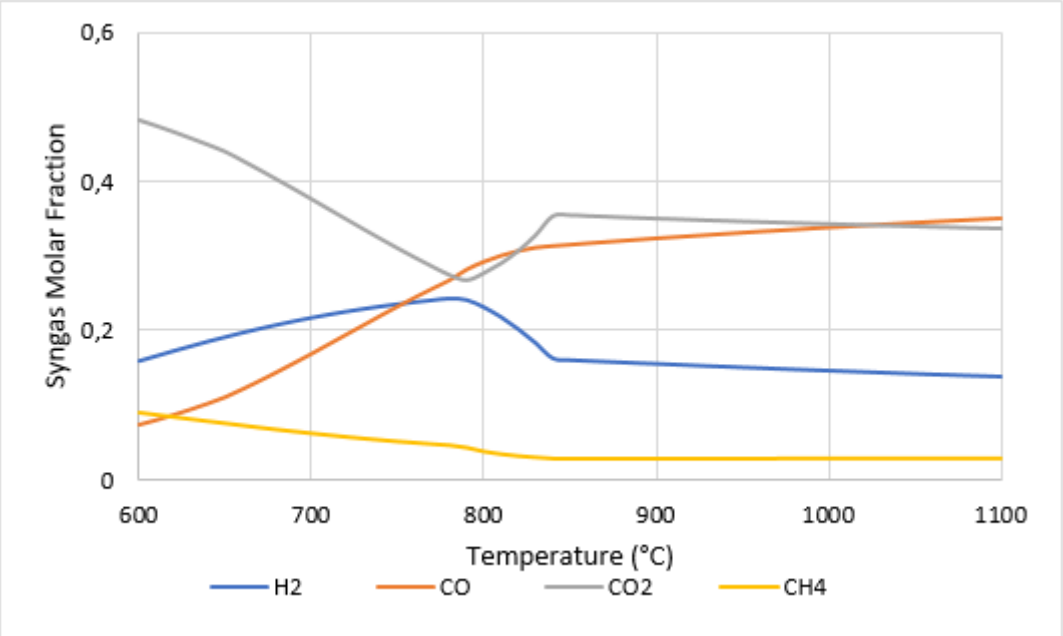
The decreasing behaviour of H_2 concentration as the CO_2 / fuel ratio increases can be expressed by the water gas shift reaction driving in the reverse direction due to the increased amount of carbon dioxide. Moreover, the increase in CO fraction until the CO_2 / fuel ratio reaches a certain point can also be associated with the water gas reaction. This ratio was 0.45 for hazelnut husk, 0.2 for Çan lignite and 0.35 for the blend. On the contrary, the concentration of the components in the syngas cannot be explained only by the reactions. The concentration of CO_2 in the syngas rises as the amount of CO_2 fed into the reactor enhances.

3.4.4.4. Effect of Temperature on Syngas Composition in Catalytic Gasification

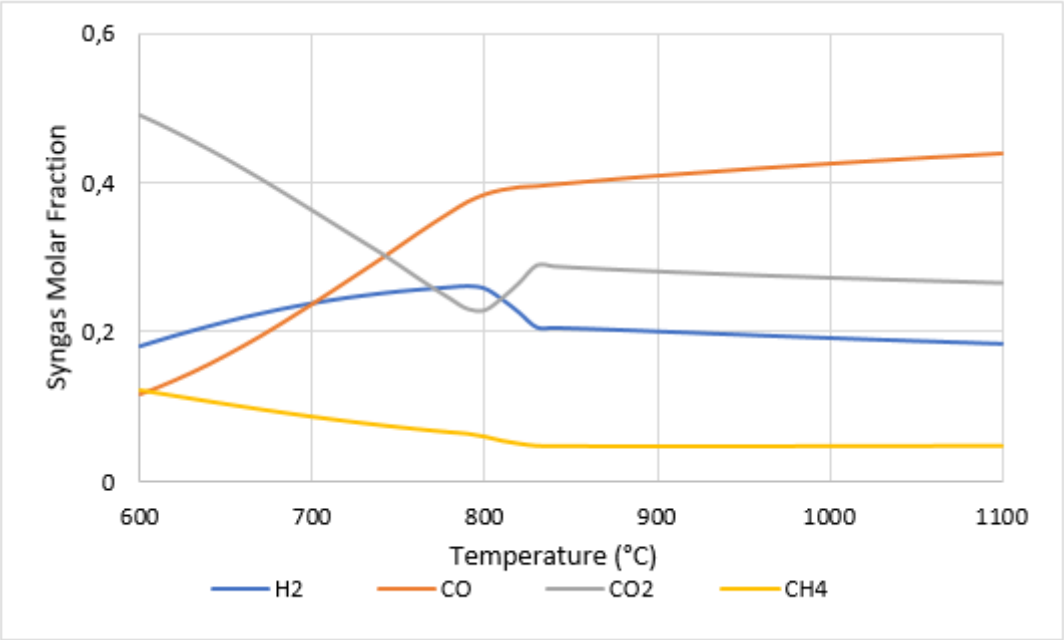
The catalyst effect on the syngas composition is given in Figure 3.17. The ratio of CaO/fuel is 0.25 for hazelnut husk, 0.5 for Çan lignite and 0.35 for the blend, and the temperature of the gasifier ranges from 600 °C to 1100 °C and pressure of the gasifier is constant at 3 bars.


0,6
0,4
0,2
0
Syngas Molar Fraction
600
700
800
900
1000
1100
Temperature (°C)
H2
CO
CO2
CH4

(a)


0,6
0,4
0,2
0
Syngas Molar Fraction
600
700
800
900
1000
1100
Temperature (°C)
H2
CO
CO2
CH4

(b)



(c)

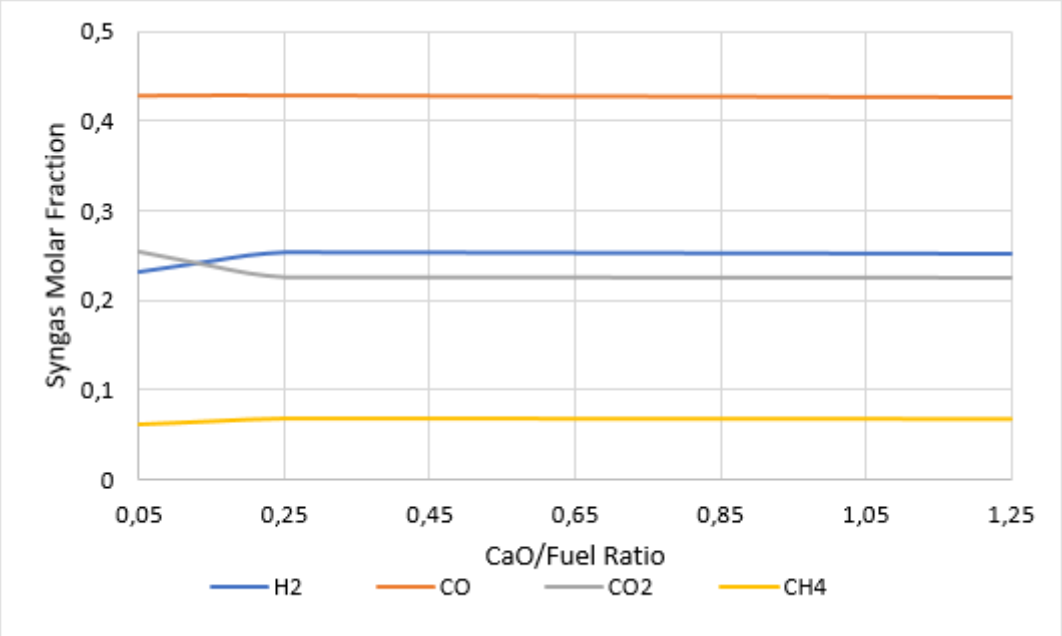
Figure 3.17 Temperature effect on syngas composition in catalytic gasification; (a) hazelnut husk (b) Çan Lignite (c) hazelnut husk & Çan Lignite blend

The H_2 composition is found higher between the 600 °C - 800 °C when the catalyst is fed into the gasifier. In the utilization of CaO catalyst for gasification, H_2 formation at temperatures lower than 800 °C indicates a great enhancement. The reactions occurred for increasing the concentration of H_2 gas due to the adsorption characteristic properties of the CaO catalyst on the CO_2. However, the H_2 gas concentration depicts an important reduce, because CaO, that holds the CO_2 and turns into $CaCO_3$, decomposes at high temperatures and emittes CO_2 gas into the gasifier when the temperature enhances, especially after 800 °C. H_2 gas generation at gasification temperatures lower than 800 °C shows a large improvement in the utilization of CaO catalyst. Because of the adsorption characteristics of the CaO catalyst on the CO_2 gas, the reactions occur in order to enhance the H_2 gas concentration. Nevertheless, the H_2 gas concentration indicates an important decrease with the temperature increases, especially after 800 °C, since CaO, which holds the CO_2 gas and turns into $CaCO_3$ form, breaks down at high temperature and releases CO_2 gas into the gasifier backwardly. CaO catalyst does not contain any side effect at high temperatures. The fast increase observed by CO and CO_2 gases can be elucidated by

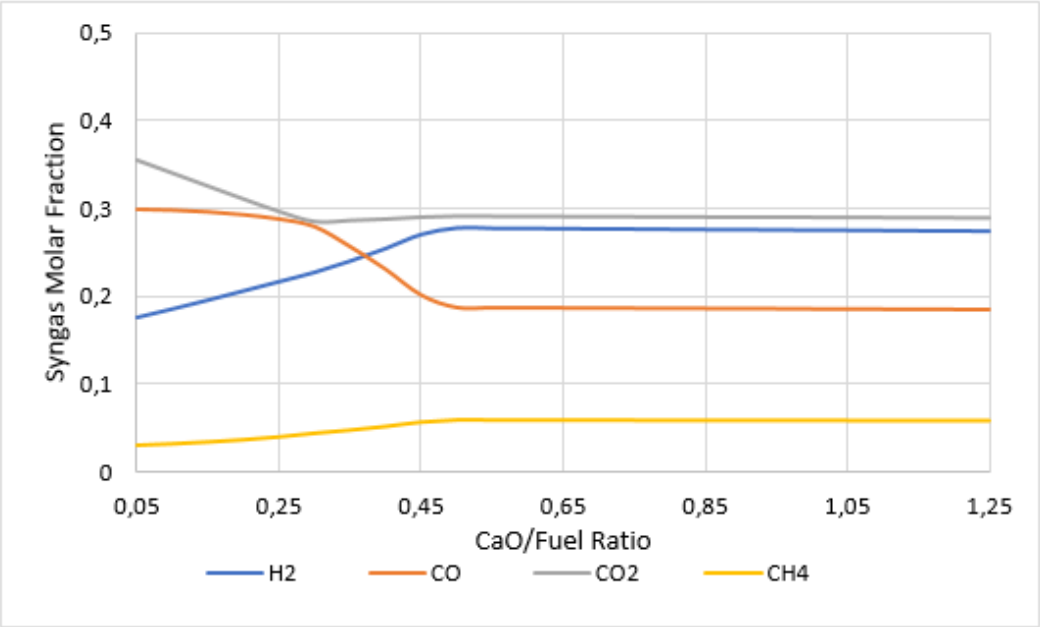
the complex reactions series in the gasifier with ignoring the catalytic effect. CaO catalyst has no effect at high temperatures.

3.4.4.5. Effect of CaO/Fuel Ratio on Syngas Composition

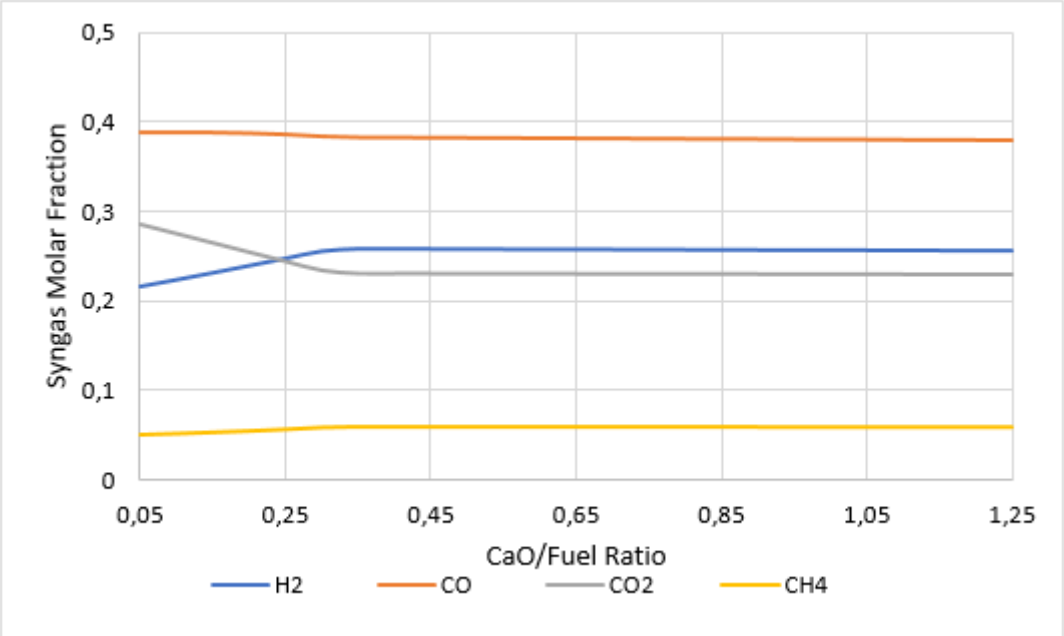
The CaO amount affects the cost and thermodynamic properties in the gasification operation. Parametric study was conducted for finding the ideal CaO/fuel ratio. Gasifier pressure is fixed at 3 bar, CO_2/fuel ratio and temperature are at maximum CO fraction for all fuels.



(a)



(b)



(c)

Figure 3.18 The effect of CaO/fuel ratio on syngas composition; (a) hazelnut husk (b) Çan Lignite (c) hazelnut husk & Çan Lignite blend

It was concluded that the enhancement of the CaO / fuel ratio from 0.05 to 1.25 enhanced the H_2 gas composition in the synthesis gas. There was not observed any important rise

in composition of H_2 after then the CaO / fuel ratio overran a certain point. This ratio was 0.25 for hazelnut husk, 0.5 for Çan lignite and 0.35 for the blend.

4. CONCLUSION

In this thesis, the assessment of the theoretical and experimental investigation co-gasification and catalytic co-gasification are discussed, and operating conditions effect on gas composition was investigated. In accordance with the data acquired:

- Thermogravimetric analysis is useful to produce data that contributes to the interpretation of the gasification reactions and to study the characteristics of biomass gasification, coal gasification and co-gasification of blend and catalytic co-gasification of blend samples.
- Biomass sample (hazelnut husk) has much higher volatile matter and much lower fixed carbon and mineral matter content compared to coal sample (Çan Lignite) resulting in different thermolysis behavior of the latter.
- TG and DTG profiles of hazelnut husk gasification, Çan Lignite gasification, co-gasification of blend and catalytic co-gasification of blend were examined in the thermal analysis results, it was observed that the catalytic co-gasification process consisted of four stages, while the other gasification processes show three stage.
- The FWO method kinetic analyses by using corresponding activation energy and against fractional mass loss indicate similar kinetic trends with and Friedman method investigation despite some variations in apparent activation.
- The highest Ea was calculated in the first stage of co-gasification of blend by both Friedman and FWO methods, while the lowest Ea value was observed by Friedman and FWO method in the second and third stage, respectively.
- The highest Ea was calculated in the fourth stage of catalytic co-gasification of blend by both Friedman and FWO methods, while the lowest Ea value was observed in the third stage.
- Modeling-based techniques ensure cost-effective and alternative access by comparison with the experimental studies to design and optimize to any complex system. Aspen plus process simulation software is beneficial for designing and optimization of system parameters.
- In this study, Aspen Plus simulation is thought to arrive chemical equilibrium with regards to thermodynamic approach.

- Methane formation reactions do not reach equilibrium in real processes, but the model reach equilibrium rapidly.
- When the gasifier temperature and the CO composition enhances, and the CO_2 composition reduces, the gasifier temperature ranges from 600 °C to 1100 °C. This can be clarified by the driving forward of the Boudouard reaction. However, when the gasifier temperature reaches at a certain point syngas composition change rate by temperature decreases. These temperatures were 760 °C for hazelnut husk, 720 °C for Çan lignite and 750 °C for the blend.
- The pressure values were changed between 1 bar and 20 bar. The concentrations of H_2 and CO gases reduce and CH_4 and CO_2 compositions enhance while the gasifier pressure rises. As a result, it was seen that operating at lower pressures was more suitable.
- The decreasing behaviour of H_2 concentration as the CO_2 / fuel ratio increases can be explained by the water gas shift reaction driving in the reverse direction due to the increased amount of carbon dioxide. It was determined that this ratio was 0.45 for hazelnut husk, 0.2 for Çan lignite and 0.35 for the blend. As the amount of CO_2 fed into the reactor increases, the concentration of CO_2 in the syngas increases.
- The H_2 formation in the system reaches the highest level between 600 °C to 800 °C in presence of catalysts. The rapid increase of CO and CO_2 concentrations can be elucidated by the lost catalytic effect and the complex reactions.
- It was observed that H_2 gas concentration in the synthesis gas increased when the CaO/fuel ratio enhanced from 0.05 to 1.25, the. After the CaO/fuel ratio exceeded a certain point, significant rise in H_2 gas concentration was not observed. This ratio was 0.25 for hazelnut husk, 0.5 for Çan lignite and 0.35 for the blend.

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