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(MASTER THESIS)

STEAM GASIFICATION OF GRAPE POMACE AND LIGNITE

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Sayın Didem ÇAĞLAYAN tarafından yüksek lisans tezi olarak sunulan “Steam Gasification of Grape Pomace and Lignite” başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 22.09.2016 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum "Steam Gasification of Grape Pomace and Lignite" başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

22 / 09 / 2016

İmzası

Didem ÇAĞLAYAN

ÖZET

ÜZÜM POSASI VE LİNYİTİN SUBUHARI GAZLAŞTIRMASI

ÇAĞLAYAN, Didem

Yüksek Lisans Tezi, Kimya Anabilim Dalı
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Eylül 2016, 44 sayfa

Bu tezde, biyokütleden hidrojen üretimi termal ve katalitik olarak su buharı gazlaştırması ile incelenmiştir. Hammadde olarak üzüm posası ve üzüm posasının 300 ºC ve 500 ºC pirolizi ile elde edilen biyokömürleri kullanılmıştır. Su buharı gazlaştırması sabit çift yataklı dikey reaktörde gerçekleştirilmiştir. Tüm denemelerde, üst yatak (biyokütle yatağı) sıcaklığı 850 ^{o}C'de sabit tutulmuş, alt yatak (katalizör yatağı) sıcaklığı ise 600 ile 850 ^{o}C arasında farklı sıcaklıklara ayarlanmıştır. Red mud, dolomit ve 10% Ni-dolomit katalizör olarak kullanılmıştır. Ayrıca, üzüm posası ve biyokömürlerin linyit ile karışımlarının gazlaştırma deneyleri yapılarak, biyokütle ilavesinin kömür gazlaştırmasındaki etkisi incelenmiştir.

Anahtar sözcükler: Üzüm posası, su buharı gazlaştırması, birlikte gazlaştırma, biyokömür, hidrojen.

ABSTRACT

STEAM GASIFICATION OF GRAPE POMACE AND LIGNITE

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MSc in Chemistry
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In this thesis, hydrogen production from biomass was investigated by thermal and catalytic steam gasification. The grape pomace and its chars which were obtained from pyrolysis at 300 ºC and 500 ºC were used as feedstock. Steam gasification experiments were carried out in a vertical fixed dual bed reactor. In all experiments, the temperature of the top bed (biomass bed) was kept stable at 850 ºC, whereas the temperature of bottom bed (catalyst bed) was set up different temperatures (600 ºC and 850 ºC). The red mud, dolomite and 10% Ni-dolomite were used as catalyst. In addition, thermal gasification of blends consisted of lignite and grape pomace (or chars) were carried out to investigate the synergic effect of addition of biomass to coal gasification was investigated.

Key words: Grape pomace, steam gasification, co-gasification biochar, hydrogen.

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SYMBOLS AND ABBREVIATIONS

Abbreviation	Explanation
FID	Flame ionization detector
G	Gram
GC	Gas chromatography
GP	Grape pomace
HCs	Hydrocarbons
Min	Minute
Ml	Milliliter
Mm	Millimeter
RGA	Refinery gas analyzer
SEM	Scanning electron microscope
TCD	Thermal conductivity detector
XRF	X-ray fluorescence

1. INTRODUCTION

The generality of the world's energy needs are provided by carbon based fossil energy. These fossil energy sources such as coal, petroleum and natural gas are nonrenewable, the decreasing fossil fuel reserves and negative environmental impact from their use made renewable and clean energy to become an increasingly important alternative. The sustainable energies and resources are solar, wind, hydroelectricity and biomass. Today, biomass essentially lingo-cellulosic biomass is widely recognized as an important renewable, inexpensive and abundant source of energy that can also be converted into biofuels and other value-added renewable products Compared to the use of fossil fuels, the use of biomass based alternatives, such as charcoal, reduces not only the emission of CO_2 but also the emission of other air pollutants such as those (i.e. NO_x and SO_x) responsible for the acid rain and photochemical smog problem and biomass can re-grow over a relatively short period of time compared with the hundreds of millions of years that it took for fossil fuels to form.

Biomass is used to meet a variety of energy needs, including generating electricity, heating homes, fueling vehicles and providing process heat for industrial facilities. The methods available for energy production from biomass can be divided into two main categories: thermo-chemical and biological conversion routes. Pyrolysis, gasification and combustion processes are thermo-chemical conversion routes of biomass (Balat et al.,2009).

2. GENERAL INFORMATION

2.1. Biomass

Biomass is the term used to biological material derived from living or recently living organisms. According to this definition, biomass for energy this is often used to mean plant based material, but biomass can evenly apply to both animal and vegetable derived material so another term for biomass is natural material derived from plant material such as wood from forests, animal manure, residues from agricultural crops and forestry processes, municipal solid wastes and sewage or industrial residues.

Biomass contains the chemical energy which is derived from the solar energy via photosynthesis. The stored energy in plants is passed to animals and people after the plants are consumed. During photosynthesis, carbon dioxide (CO_2) and water (H_2O) converted to organic compounds, loosely termed carbohydrates and another produced is oxygen (O_2). Biomass is comprised of approximately 75% carbohydrate polymer. The most common trapped energy in the biomass materials used for produce energy is called bioenergy and it is such a widely utilized source of energy namely the fourth largest source of energy in the world at the same time providing about 14% of the world's basic energy supply because of its low cost and indigenous nature. In the short term, this proportion will raise because of biomass benefits such as lack of shortage sources, production clean and sustainable energy hereby positive environmental impact. This is also alternative and new way to dispose for residues because the disposal of wastes is one of main problems of the world.

Biomass includes a wide range of organic materials. These organic materials are generally composed of cellulose, hemicellulose, lignin, lipids, proteins, simple sugars and starches. Cellulose, hemicellulose, and lignin are three main components, among these compounds (Zhang et al., 2010).

2.1.1 Cellulose

Cellulose is a natural straight chain polymer, a long chain made by the linking of smaller sugar molecules that gives wood its remarkable strength. It is the main component of plant cell walls and comprises 40-50 wt % of dry biomass.

Cellulose is a polysaccharide consisting of a linear chain of several hundred to many thousands of β-1,4 linked D-glucose units (Figure 2.1). Its molecule formula is $(C_6H_{10}O_5)_n$ and the degree of polymerization is shown with n and it determines the size of the cellulose molecule. The decomposition temperature of Cellulose is 300 ºC. Cellulose is broken down into monosaccharide D-glucose after complete hydrolysis, whereas upon partial hydrolysis, cellulose is broken into cellobiose (glucose dimer), cellotriose (glucose trimer), and cellotetrose (glucose tetramer).

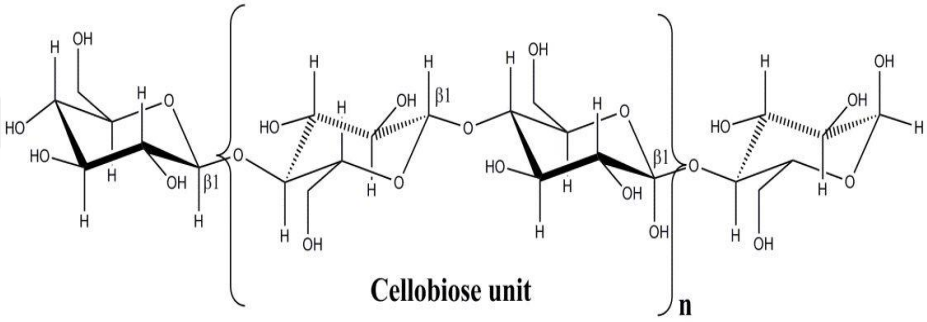

Figure 2.1 Structure of cellulose.

Cellulose consists of crystalline because of the strong hydrogen bonds that occur between cellulose chains and it does not dissolve in water or common solvents. Also cellulose is great fiber. It does not exist alone in nature, it is exist embedded in the hemicellulose, pectin, protein and other polymers matrix.

2.1.2 Hemicellulose

Hemicellulose is another component of lignocellulosic biomass and it is consist of five-carbon sugar (D-xylose and L- arabioz) and six-carbon sugars (D-galactose, D-glucose and D-mannose) with uronic acid, 4-O methyl glucuronic

acid and galacturonic acid in the structure (Figure 2.2). In contrast to cellulose, which is a polymer of only glucose, hemicellulose is a polymer of many different sugar monomers. Hemicellulose has a random, amorphous structure with little strength and it soluble in water. Hemicellulose has the most sensitive structure to heat and its active decomposition temperature is 200-260 ºC. It is derived decomposition of cellulose.

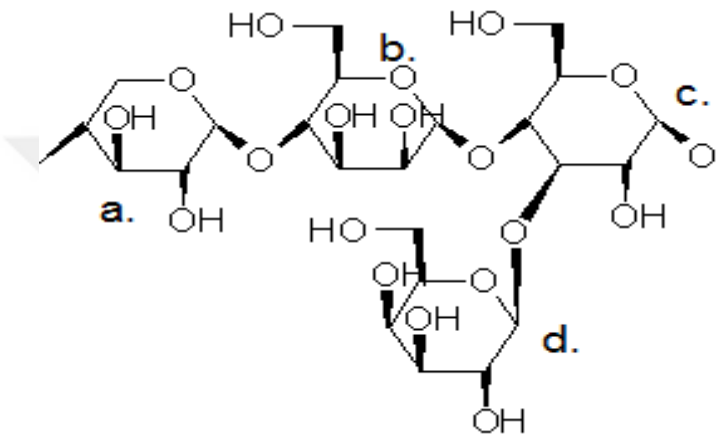

Figure 2.2 A part of chemical structure for hemicellulose **a.** xylose**, b.** mannose**, c.** glucose, **d.** galactose.

2.1.3 Lignin

Lignin, which is a complex polymer of aromatic alcohols found in the cell walls of especially woody biomass and corresponding approximately to the formula is $(C_{31}H_{34}O_{11})_n$. It is not a carbohydrate but its functions very close to carbohydrate. After cellulose, it is the second abundant organic polymer and renewable carbon source on Earth. It is composed of three different phenyl propane monomers (Figure 2.3). Lignin contains both hydrophilic and hydrophobic groups. Its decomposition temperature is higher than cellulose and hemicellulose (280-500 ºC) because of lignin has a three-dimensional and complicated structure.

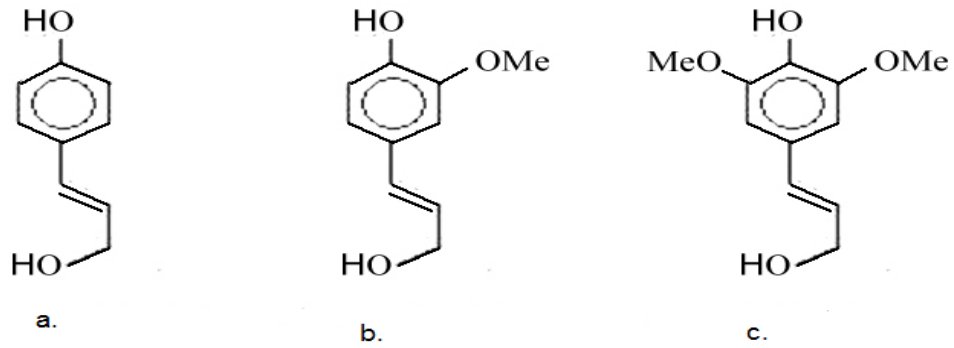

Figure 2.3 The three monomeric phenyl propane units in lignin; **a.** coumarly alcohol, **b.** coniferyl alcohol **c.** syringyl alcohol.

2.1.4 Extractives

Extractives are other lignocellulosic biomass component which determines the characteristic of biomass like odor or color and that can be extracted from biomass using suitable solvents. These can be extracted from biomass with polar solvents (such as water, methylene chloride, or alcohol) or nonpolar solvents (such as toluene or hexane). The examples of extractives include fats, waxes, alkaloids, proteins, phenolic, simple sugars, pectin, mucilage, gums, resins, terpenes, starches, glycosides, saponine, and essential oils.

2.1.5 Inorganic Minerals

Biomass also includes a small amount of inorganic minerals such as ash in addition to the organic compounds. Ash content consists of mainly metal elements such as Ca, K, P, Mg, Si, Al, Fe and Na etc. (mainly oxides and carbonates of metals). Those inorganic minerals can serve as catalysts in thermochemical conversion processes of biomass.

2.2. Conversion of Biomass

A wide range of technologies and processes exist of convert to energy stored in biomass to useful forms of energy. Biomass can be converted into three main products: power/heat generation, transportation fuels and chemical feedstock. Factors that influence the choice of conversion process are: the type and quantity of biomass feedstock; the desired form of the energy, i.e. end-use

requirements; environmental standards; economic conditions; and project specific factors. In many situations it is the form in which the energy is required that determines the process route followed by the available types and quantities of biomass**.** But it needs to be considered that the moisture contents of biomass have an important influence on the type of process that will be followed. However intrinsic properties of biomass such as moisture contents of biomass determine the type of conversion process that will be followed.

Conversion processes are available or under development for both wet and dry feedstoks. Examples of wet biomass are: sewage sludge, sugar solutions, algae suspensions, waste streams from biomass processing or from bio refineries. Dry biomass commonly has low moisture content (less than 30 wt %). Examples of dry biomass are: wood, straw, or other sun dried waste. Of course wet biomass can be dried with energy from other sources, but this is not always the most efficient or economical way to operate**.**

The main two types of conversion processes are thermochemical, biochemical and physical- chemical processes conversion methods to convert biomass into energy. Thermochemical process is used for dry biomass conversion and also biochemical method usually prefers wet biomass conversion (Duman, 2009; Pala, 2013).

2.2.1. Biochemical Conversion of Biomass

Biochemical conversion of biomass involves use of bacteria, microorganisms and enzymes to breakdown biomass into alcohols or oxygenated products. The main biochemical technologies are anaerobic digestion (or biomethanation) and fermentation.

2.2.1.1. Anaerobic Digestion

Anaerobic digestion is the natural biological process to decomposition of organic waste in the absence of oxygen to produce biogas. Anaerobic digestion is widely used for the production of methane- and carbon-rich biogas from crop

residues, food scraps, and manure (human and animal). Anaerobic digestion is frequently used to reduce emissions from landfills and in the treatment of wastewater.

Anaerobic digestion involves a multi-stage process over a period ranging from a few days to several weeks. First, bacteria are used in hydrolysis to break down carbohydrates into forms digestible by other bacteria. The second set of bacteria converts the resulting sugars and amino acids into carbon dioxide, hydrogen, ammonia and organic acids. Finally, still other bacteria convert these products into methane and carbon dioxide. Mixed bacterial cultures are characterized by optimal temperature ranges for growth. These mixed cultures allow digesters to be operated over a wide temperature range, for example, above 0 ºC and up to 60 ºC. When functioning well, the bacteria convert about 90% of the biomass feedstock into biogas (containing about 55% methane), which is a readily useable energy source.

Solid remnants of the original biomass input are left over after the digestion process. This by-product, has many potential uses. Potential uses include fertilizer (although it should be chemically assessed for toxicity and growth-inhibiting factors first), animal bedding and low-grade building products like fiberboard (Wisconsin Grasslands Bioenergy Network, 2016).

2.2.1.2. Fermentation

Fermentation is a metabolic process that converts sugar to acids, gases or alcohol under anaerobic conditions. This process is used commercially on large scale to produce ethanol. Yeast or bacteria are added to the biomass material, which feed on the sugars to produce ethanol (an alcohol) and carbon dioxide. The ethanol is distilled and dehydrated to obtain a higher concentration of alcohol to achieve the required purity for the use as automotive fuel. The solid residue from the fermentation process can be used as cattle-feed and in the case of sugar cane; the bagasse can be used as a fuel for boilers or for subsequent gasification (Biomass Innovation Center, 2016).

2.2.3. Thermochemical Conversion

Thermochemical conversion is the application of heat and chemical processes in the production of energy products from biomass. Heating temperature can be changed over a wide range of 300 to 1000 ºC in this process and the thermochemical process involves multiple stages. Firstly, converting solid biomass into gases, secondly, the gases are condensed into oils and finally, oils are conditioned and synthesized to produce syngas (Biomass Innovation Center, 2016).

Choice of conversion process depends upon the type and quantity of biomass feedstock, the desired form of the energy, i.e., end use requirements, environmental standards, economic conditions and project specific factors. The main processes, the intermediate energy carriers and the final energy products resulting from thermo-chemical conversion are illustrated in the flowchart shown in Figure. 2.4.

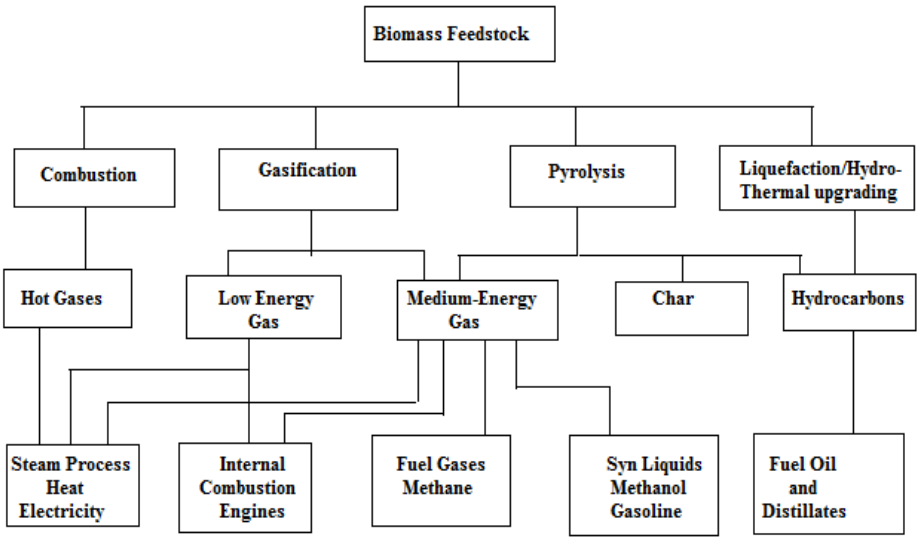

Figure 2.4 Main processes of the thermochemical conversion of biomass (McKendry,2002).

2.2.3.1 Combustion

Combustion of biomass is the oldest known and most widely used controllable energy supply and contributes to over 97% of bioenergy production in the world. The simply means of biomass combustion is burning organic material. Combustion is a process which is the partial or total oxidation of carbon and hydrogen converts the stored chemical energy in biomass as heat in burners, boilers, internal combustion turbines and engines. Combustion of biomass is a complex process that consists of sequential homogeneous and heterogeneous reactions. The main stages are drying, pyrolysis and reduction, gasification and combustion of volatile gases and char.

Combustion of biomass produces hot gases at temperatures around 800–1000 ºC. It is feasible to burn any type of biomass but in practice combustion is possible only for biomass with a moisture content <50%, unless the biomass is pre-dried. High moisture content biomass is more convenient to biological conversion processes. The scale of combustion plant ranges from very small scale (e.g. for domestic heating) up to large-scale industrial plants in the range 100–3000 MW. Net bio-energy conversion efficiencies for biomass combustion power plants range from 20% to 40%. The higher efficiencies are obtained with systems over 100 MWe or when the biomass is co-combusted in coal-fired power plants (McKendery, 2002).

2.2.3.2. Pyrolysis

Pyrolysis is the thermal decomposition of biomass occurring in the absence of oxygen. It is the fundamental chemical reaction that is the precursor of both the combustion and gasification processes and occurs naturally in the first two seconds. The products of biomass pyrolysis include biochar, bio-oil and gases including methane, hydrogen, carbon monoxide, and carbon dioxide. Depending on the thermal environment and the final temperature, pyrolysis will yield mainly biochar at low temperatures, less than 450 ºC, when the heating rate is quite slow, and mainly gases at high temperatures, greater than 800 ºC, with rapid heating

rates. At an intermediate temperature and under relatively high heating rates, the main product is bio-oil.

Pyrolysis can be performed at relatively small scale and at remote locations which enhance energy density of the biomass resource and reduce transport and handling costs. Heat transfer is a critical area in pyrolysis as the pyrolysis process is endothermic and sufficient heat transfer surface has to be provided to meet process heat needs. Pyrolysis offers a flexible and attractive way of converting solid biomass into an easily stored and transported liquid, which can be successfully used for the production of heat, power and chemicals (Salman, 2016).

There are three primary types of pyrolytic reaction, which are differentiated by temperature and the processing or residence time of the biomass. Conventional or slow pyrolysis is characterized by slow biomass heating rates, low temperatures and, lengthy gas and solids residence times. Depending on the system, heating rates are about 0.1 to 2 ºC per second and prevailing temperatures are around 500 ºC. Gas residence time may be greater than five seconds while that of the biomass can be range from minutes to days. During conventional pyrolysis, the biomass is slowly devolatilized; hence, tar and char are the main products. After the primary reactions have occurred, re-polymerization or recombination reactions are allowed to take place. Flash pyrolysis is characterized by moderate temperatures exist (400-600 ºC) and rapid heating rates (>2 ºC/s). Vapor residence times are usually less than two seconds. Compared to slow pyrolysis, considerably less tar and gas are produced. However, the tar and oil products are maximized. The only difference between flash and fast pyrolysis (more accurately defined as thermolysis) is heating rates and hence residence times and products derived. Heating rates are between 200 and 105 ºC per second and the prevailing temperatures are usually higher than 550 ºC. Due to the short vapor residence time, products are high quality, ethylene-rich gases that could subsequently be used to produce alcohols or gasoline. Notably, the production of char and tar is considerably less during this process (Sadaka, 2016).

The solid product of the thermal decomposition of the organic matter present in biomass under controlled and oxygen-free or oxygen-limited conditions

(usually pyrolysis) is called biochar. Generally slow pyrolysis used to maximize char yields (generally up to 35 wt% on dry feedstock weight basis). Biochar is a carbon-rich and stable material and it has many benefits which is added in soils for its amendment, modifying and improving the soil functions and hereby improving crop yields. In addition to biochar is increased soil carbon sequestration and thus decreased climate change. The benefits of the use of biochar had 2000 years old history and today, the importance of biochar is increasing because of its production technology is relatively inexpensive and it has widely applicable.

2.2.3.3. Gasification

Gasification is the thermochemical conversion of biomass or fossil fuel based carbonaceous materials into a combustible product gas with the use of controlled amount of a gasifying agent or agents, such as steam, air and carbon dioxide (CO_2) at high temperatures, typically in the range 800–900 ºC. The product gas mixture is called syngas and it is a mixture of mainly carbon monoxide (CO) and hydrogen (H_2). In addition to these, usually carbon dioxide (CO_2), methane (CH_4) and higher hydrocarbons such as ethylene and ethane, propane and propylene are other components arising from gasification. Syngas can be burnt directly and also used as a fuel for gas engines and gas turbines to produce heat and electricity or is converted via the Fischer-Tropsch process into liquid hydrocarbons or used as a feedstock in the production of chemicals e.g. methanol (Bremaud et al., 2005; McKenderey, 2001). Thermochemical conversion process can be expressed as:

Biomass + heat + steam (or O_2) → H_2 + CO + CO_2 + CH_4 + light and heavy hydrocarbons + char + tar + ash.

Gasification processes consists of four steps; drying, pyrolysis, oxidation and reduction steps (Couto et al. 2013). The gasification process is applicable to biomass consist of moisture content ranging from 5 to 35%. In drying step, the water is removed and converted into steam at temperatures above 100 ºC and there is not any kind of decomposition. In pyrolysis step; thermal decomposition

processes involves when heating solid carbonaceous feedstock, usually up to 700 ºC. The volatiles in the feedstock are vaporized in primary reactions and leaving a residue consisting of char and ash. When volatiles liquefy at low temperatures, tar may also be produced. In oxidation step, char and volatiles are combusted with oxygen (O_2) of the essential gasifying agents (steam or CO_2) to producing carbon monoxide (CO). Oxidation reaction is exothermic, and this released heat is used for reduction reactions. Finally, reduction step is mainly gasification reaction and reduction reactions are endothermic. Char, tar, and light hydrocarbons are gasified with CO_2 and steam to produce mainly composed of carbon monoxide (CO), hydrogen (H_2), and methane (CH_4), which is called synthetic gas (syngas). The important gasification reactions as follows (National Energy Technology Laboratory, 2016):

1.	$C + H_2O \leftrightarrow CO + H_2$	Water-gas reaction	ΔH_{R1}= +131 MJ/kmol
2.	$C + CO_2 \leftrightarrow 2CO$	Boudouard reaction	ΔH_{R2}= +172 MJ/kmol
3.	$C + 2H_2 \leftrightarrow CH_4$	Methanation reaction	ΔH_{R3}= +75MJ/kmol
4.	$CO + H_2O \leftrightarrow CO_2 + H_2$	Water-gas-shift reaction	ΔH_{R4}= -41 MJ/kmol
5.	$CH_4 + H_2O \leftrightarrow CO_2 + 3H_2$	Steam-methane reforming reaction	ΔH_{R5} =+206 MJ/kmol

The most effective way to increasing hydrogen gas production is the steam gasification (Kim et al., 2014).

The gasification products are varied depending on the type of biomass, type of reactor, the temperature, the catalyst, and gasifying medium. A wide variety of catalysts such as dolomite, potassium mineral, nickel-based compounds have been used in gasification processes (Hamad et al., 2016).

One of the main issues in gasification of biomass is to deal with the tar formation. Tar is a complex mixture of condensable hydrogen which includes single ring to 5-ring aromatic compounds along with other oxygen containing hydrocarbons and complex the polycyclic aromatic hydrocarbons (PAHs). Currently, two methods are available to minimize tar formation: (i) treatments

inside the gasifier (primary methods), (ii) hot gas cleaning after the gasifier (secondary methods). Although secondary methods are proven to be effective, treatments inside the gasifier are getting much attention due to economic benefits. In primary methods, the operating parameters such as temperature, gasifying agent, equivalence ratio, residence time and catalytic additives play important roles in the formation and decomposition of tar. Pilot-scale tests have shown that catalytic cracking of tars can be very effective. Tar conversion in excess of 99% has been achieved using dolomite, nickel-based and other catalysts at elevated temperatures of typically 1075–1175 K (Balat et al., 2009). Catalysts not only decrease the tar content, besides improve the gas product quality and conversion efficiency.

Another problem of biomass gasification is the formation of ash that may cause deposition, sintering, slagging, fouling and agglomeration. To resolve the ash-associated problems, fractionation and leaching of feedstock have been employed to reduce ash formation inside the reactor. Though fractionation is effective for ash removal, it may deteriorate the quality of the remaining ash (Ni et al., 2006).

2.2.4. Types of Gasifiers

Gasifiers are the cylindrical stainless steel reactors in which gasification reactions take place. The sequence of reactions, gasifying agents, and stream configurations determine the type of reactor. The sequence of reactions for solid and gas species within the gasifier is the main difference of between reactor types. The steps for solid feed are drying, pyrolysis, char gasification, and ash melting, for some gasifier types (Mahinpey et al., 2016). Mainly two types of gasifiers in which depends upon type of fuel used, air introduction in the fuel column and type of combustion bed are fixed bed reactor and fluidized bed reactor with variations within each type.

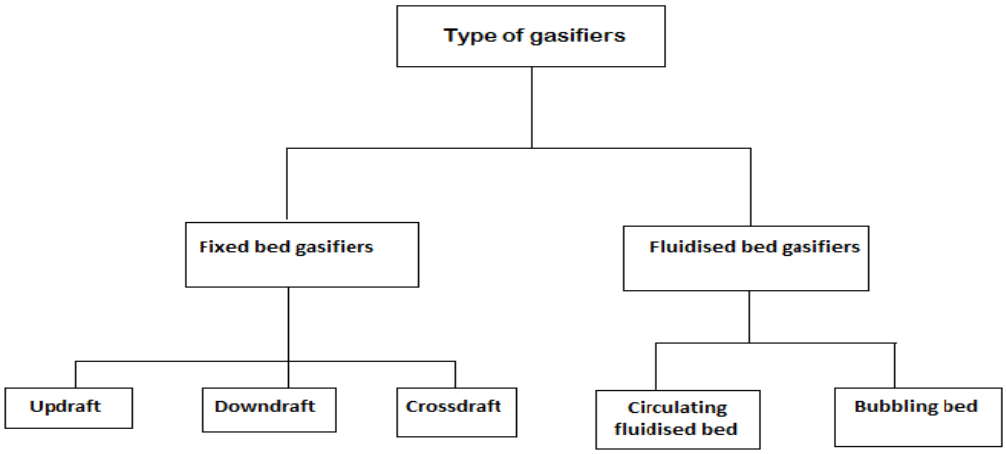

Figure 2.5 Gasifiers types (Panwar et al., 2012).

Fixed bed gasifiers are the oldest and simplest design types of gasifier. They are most suitable for biomass gasification. Fixed-bed gasifiers involve reactor vessels in which the biomass material is either packed in or moves slowly as a plug, with gases flowing in between the particles. Fixed-bed gasifiers are frequently fed from the top of the reactor (Balat et al., 2009). They can be designed in updraft, downdraft, and crossdraft configurations. In the updraft gasifier the feed is introduced at the top and the air at the bottom of the unit via a grate. In the downdraft gasifier, the feed and the air move in the same direction. In a cross-flow gasifier the feed moves downwards while the air is introduced from the side, the gases being withdrawn from the opposite side of the unit at the same level. Simple design is advantage and producing a low calorific value gas with a high tar contents is disadvantage of fixed bed gasifiers (McKendery, 2002). Mainly smaller-scale gasifiers are fixed-bed design.

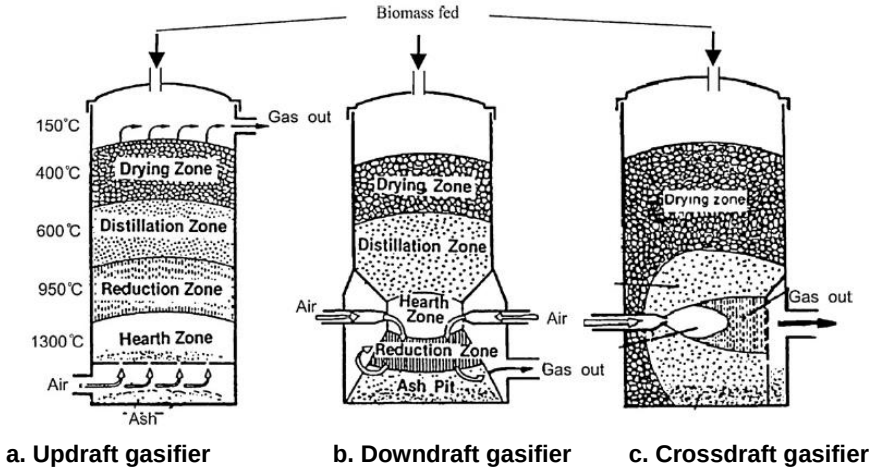

Figure 2.6 Fixed bed gasifier configurations (Panwar et al., 2012).

In fluidized bed gasifiers, the feed is brought into an inert bed of fluidized material such as sand. Fluidized bed gasifier has been used extensively for coal gasification from many years (Panwar et al., 2012). Fluidized-bed gasifiers can also be further classified into bubbling fluidized gasifiers and circulating fluidized gasifiers. In a bubbling fluidized gasifier, air is injected from the bottom of a grate, above which the moving bed is mixed with the feedstock. The bed temperature is maintained at 700–900 ^{o}C. Feedstock is pyrolyzed and cracked through contact with the hot bed material. In a circulating fluidized gasifier, the hot bed material is circulated between the reactor and a cyclone separator. During this circulation, bed materials and char go back to the reactor, while the ash is separated and removed from the system.

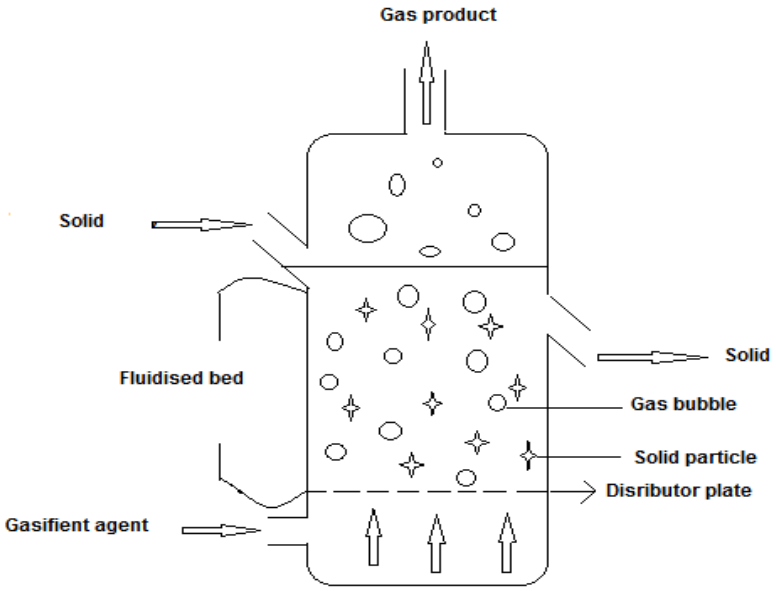

Figure 2.7 Fluidized bed gasifier.

The main advantages of fluidized-bed gasification over fixed bed gasification is the uniform distribution of temperature within the reactor and fluidized-bed gasifiers can be sized effectively for middle or large scale facilities (Zhang et al., 2010).

3. LITERATURE REVIEW

Gasification of biomass has attracted considerable attention as a renewable energy source in the last two decades. The process parameters which have the main influence on the products are the gasification temperature, biomass types and effect of catalyst. Many researchers have studied gasification of biomass to produce hydrogen.

Steam gasification is considered one of the most effective, efficient technologies of hydrogen production from biomass. Steam gasification offers the highest hydrogen yield, of all the thermochemical processes. It provides a promising option for sustainable hydrogen production since biomass is plentiful throughout the world (Parthasarathy et al., 2015). Nipattummakul et al. (2010) presented that steam gasification increased the hydrogen yield threefold as compared to air gasification. Franco et al. (2003) reported that the use of pure steam is more economical, and favors more hydrogen yield compared to other conventional gasifying agents. Umeki et al. (2009) reported water-gas shift reaction vital for hydrogen production which could be enhanced by steam gasification.

The factors which influence the yield of hydrogen in steam gasification were also investigated. Biomass feed particle size, gasification temperature, addition of catalyst are some of the important factors. Luo et al. (2009) in their study reported that decrease in particle size improved carbon conversion efficiency and hydrogen yield. Lasa et al. (2011) confirmed that with increase in temperature, hydrogen yield increased significantly. The effect of catalyst in hydrogen production of biomass is the one of the efficient studies. Ni et al. (2006) in their work demonstrated that dolomite, Ni-based catalysts and alkaline metal oxides catalysts are best for gasification reactions.

Wei et al. (2007) investigated characteristics of steam gasification of two kinds of biomass (legume straw and pine sawdust) at high heating rate (in the order of 1000 ºC s−1). The effects of steam/biomass (S/B) mass ratio (0.0–1.0 g/g) and reactor temperature (750–850 ºC) on the product yields and the

compositions of product gas were determined. They reported that gas yields and the amount of H_2 in the gas increased with reactor temperature, and presence of steam increased the gas yields. They also studied effect of catalyst for steam gasification of biomass. Dolomite was revealed good performance, and the consequential increased in the production of gases.

Waheed et al. (2015) investigated hydrogen production from the steam catalytic gasification of bio-char in a high temperature fixed bed reactor. Bio-char obtained from the pyrolysis of sugar cane bagasse and the catalysts used were Ni-dolomite, Ni-MgO and Ni-Al_2O_3, all with 10% nickel loading. The hydrogen yields without of a catalyst at a gasification temperature of 950ºC were 25.24 mmol.g^{-1} of sugar cane bagasse and 100.97mmol.g^{-1} of bio- char. However, the presence of the Ni-MgO and Ni-Al_2O_3 catalysts produced significantly improved hydrogen yields of 178.75 and 187.25 mmol.$g^{-1}$of bagasse char respectively at 950 ºC. The hydrogen yield from the char with the Ni-dolomite only showed a small increase in hydrogen yield (112.36 mmol.g^{-1}).This higher H_2 yield with Ni-Al_2O_3 catalyst because of it has larger surface area. When the temperature was increased from 750 to 850 ^oC, the H_2 yield sharply increased from 45.30 to 120.84mmol.g^{-1} of bagasse char with Ni-Al_2O_3 catalysts and the highest hydrogen yield from bio-char with Ni-Al_2O_3 catalysts was obtained at 950^oC (187.25mmol.g^{-1}). It has been suggested that high temperature steam gasification of char is recommended for the production of hydrogen.

Duman et al. (2014) studied steam gasification of safflower seed cake was carried out using a flow-type reactor in a two steps process at two different catalytic bed temperatures (600-700 ºC) in the presence of CeO_2–Fe_2O_3 catalysts with different CeO_2–Fe_2O_3ratios. The effects of both catalyst and the temperature of catalytic bed on the tar decomposition and the gaseous product yield were investigated. The temperature of up bed (biomass bed) was selected as 850 ºC in the present study. In their experimental system; the decomposition of biomass with steam proceeds is in the first step pyrolysis of biomass and evolution of volatile matters including tars at 200-500 ºC; and in the second step steam gasification of char at 500-850 ºC in the up bed (biomass bed) for non-catalytic gasification; additionally in the presence of catalyst, reforming of tar on the

catalyst, the water–gas shift reaction (WGSR) on the catalyst, and the steam–iron reaction are possible. The gas product was collected in two gas sample bags (between these temperatures 200-500 and 500-850 ºC) and analyzed with a gas chromatography. When the temperature of catalyst bed was increased from 700 to 850 °C for the non-catalytic gasification of biomass, the total gas yield increased and tar conversion increased from 53.8% to 83.3%. Furthermore, they investigated catalyst effect of gas product yield and the temperature programmed in the up bed at 200-850 ºC and in the down bed (catalyst bed) at the constant temperatures of 600 and 700 ºC at a SV of 1.85 × 104 h^{-1}. Temperature had considerable effects on the tar conversion: tar conversion increased when the bed temperature was increased from 600 ºC to 700 ºC, but the yield of hydrogen is dependent on the catalyst type. The tar decomposition was completed on 50% CeO2–50% Fe_2O_3 at 700 ºC. The highest H_2 yield was derived with 90% CeO2–10% Fe_2O_3 (1465 cm^3/g) at 600 ^oC and 50% CeO2–50% Fe_2O_3 (1492 cm^3/g) at 700 °C.

Howaniec et al (2011) studied steam co-gasification of coal (Polish hard coal) and biomass (Salix Viminalis) blends in a fixed bed reactor under atmospheric pressure and at the temperature of 700, 800 and 900ºC. The effect of co gasification of coal/biomass blends of 20, 40, 60 and 80% w/w biomass content was investigated. A synergy effect in the co-gasification for all coal and biomass ratio studies, increasing the hydrogen product yield, when compared to coal and biomass gasification product yields results, was observed at all studied temperatures. The observed synergy effect was attributed to the catalytic effect of K_2O present in blend ash (6-10% wt). Another synergy effect was in co-gasification of blends of 20% w and 40% w content of biomass (the highest hydrogen yield and total product gas yield) additionally increasing the biomass content to 60% w and 80% w resulted in a slight decrease hydrogen yield was derived, when compared to the experiments of coal and biomass gasification separately. However, compared to fossil fuel based energy production processes, higher ratio of biomass in co-gasification is an attractive option in terms of CO_2 emission and increase in hydrogen production.

Sharma et al. (2015) studied co-gasification of coal and biomass. Gasification studies were conducted using a downdraft gasification system with different fuel blends, and varying reactants (air, air + steam). The performance of these blends was compared with only biomass and coal. Biomass gasification results in higher percentage of H_2, CO, CO_2 than coal gasification. Steam was found beneficial in increasing the carbon conversion, and H_2 production was found to improve with steam addition.

Hamad et al. (2015) studied catalytic gasification of biomass to production of hydrogen rich gas of bench scale using oxygen as the gasifying agent. The experimental studies are gasification of different types of biomass (cotton stalk, corn stalks and rice straw) with different catalysts (Mary clay, dolomite, calcium hydroxide and calcined cement kiln dust) at different temperatures (700-850ºC). Calcium hydroxide and calcined cement kiln catalysts resulted in higher hydrogen yields, 45 vol% and 39 vol%, respectively from the gasification of cotton stalks. As the gasification temperature increased from 750 to 850ºC, gas yield increased from 0.7 to 1.237 m^3/kg. The observed trends can be explained as follows; first, more unconverted volatiles are released at higher temperature; second, higher temperature helps reactions such as Boudouard and methanation, since they are endothermic reactions; and third, higher temperature favors the cracking and reforming of tar. According to Le Chateliers' principle, higher temperatures favor the reactants in the exothermic reactions and favor the products in endothermic reactions. Since the main reactions are endothermic, they are favored by increasing temperature. Higher temperatures significantly resulted in higher H_2 and CO contents. The optimum conditions observed for the gasification of cotton stalks were then applied to rice straw and corn stalks. Corn stalks give the highest reactivity (highest carbon conversion) towards applied gasification conditions while rice straw was the lowest. However, the gasification efficiency and hydrogen content was the highest for cotton stalks (H_2 yield 39.9 vol%), even when no catalyst was used (gas yield 1.1 m^3/kg). This is because result of proximate and elemental analysis; cotton stalks have higher carbon (44.8 %) content and lower ash content (4.28 %) compared to other biomass.

Yan et al. (2010) studied steam gasification of char from biomass fast pyrolysis in a fixed-bed reactor to produce hydrogen-rich gas and investigated influence of temperature and steam on hydrogen yield and syngas composition. The feedstock material used in this study was biomass char, which was produced by fast pyrolysis liquefaction of pine sawdust in a fixed-bed reactor, at final pyrolysis temperature of 500 ^{o}C (ultimate analyses of biomass char are shown it has high carbon content 70.68 wt.%). The results showed that both high gasification temperature and entry of proper steam led to higher yield of dry gas and higher carbon conversion efficiency. The highest hydrogen yield was obtained at the gasification temperature of 850 ºC and steam flow rate of 0.165 g/min/g biomass char (52.41 v.%).

4. MATERIALS AND METHODS

4.1. Materials

4.1.1. Feedstocks

In this study, grape pomace (GP), grape pomace biochars (GP300 and GP500), lignite and blends (1:1) containing lignite-GP, lignite-GP300 and lignite-GP500 were used as a feedstock in gasification experiments. All feedstocks were ground and sieved to 0.1-1.0 mm sieve in order to obtain a homogenous sample.

Grape pomace was kindly provided by Yazgan Şarapçılık, Izmir, Turkey. The moisture content of grape pomace was 60 % wt as received. It was dried first in air and then in oven at 60 ºC for 24 hours. Grape pomace biochars were obtained from pyrolysis at different temperatures (in Section 4.2.1) and then ground and sieved; they were also dried in oven. Some properties of grape pomace and grape pomace biochars and some inorganic contents in ash of grape pomace, and also some properties of lignite are given are in Table 4.1, Table 4.2, Table 4.3, respectively.

Table 4.1 Some properties of GP, GP300 and GP500.

	GP	**GP300**	**GP500**
Elemental analysis (dry, wt %)			
C	51.3	63.1	69.4
H	5.9	5.3	2.7
N	2.1	2.6	2.5
S	-	-	-
O	35.3	22.2	11.8
Proximate analysis (dry, wt %)			
Ash	5,4	6,8	14,3
Volatile matter	72.6	50,7	36,2
Fixed Carbon	21.9	40,5	48,6
HHV, MJ/kg	20.0	25,9	28,7

Table 4.2 Inorganic contents in ash of grape pomace, wt%.

K	36.04
Si	19.10
Ca	9.69
Fe	1.22
Mg	1.07
Na	0.65
Al	0.48
Mn	0.03

Table 4.3 Some properties of lignite.

Parameters	Coal	Dry coal in the air	Dry coal
Moisture %	14.40	12.79	-
Ash %	18.59	18.94	21.76
Volatiles %	35.62	36.29	41.61
Fixed carbon %	31.39	31.96	36.67
Total sulfur %	0.80	0.81	0.93
Low calorific value (kcal/kg)	4072	4160	4859
High calorific value (kcal/kg)	4330	4414	5065

4.1.2. Catalysts

In this study, three different catalysts were used; red mud, dolomite ($CaMg(CO_3)_2$) and 10% Ni-dolomite.

Red mud is a waste product obtained in the industrial production of aluminum. In this study, red mud catalyst was used after activation to increase the

surface area of the catalyst and remove to soluble alkali metal ions. For activation, the red-mud was boiled in HCl solution for 20 min. After that, the solution was diluted with distillated water and then the NH_3 solution was added until pH of 8. The precipitate obtained was washed, dried at 105 °C and finally calcinated at 700 °C for 2h. Table 4.4 shows the inorganic contents of red mud before and after activation.

Table 4.4 XRF results of red mud before and after activation, wt% .

	Fe	**Na**	**Mg**	**Al**	**Si**	**S**	**K**	**Ca**	**Ti**
Red mud before activation	49.5	12.7	0.5	14.5	12.0	0.2	0.5	3.8	5.9
Red mud after activation	59.6	0.2	0.3	17.4	12.6	0.1	0.1	2.2	6.6

After activation, the BET surface area of red mud increased from 15 to 158 m²/g. Dolomite was used as received (without washing, etc.). 10% Ni-dolomite catalyst was prepared by impregnation method. Thus, the compound containing Ni was dissolved in water, and added on dolomite. After that the obtained mixture was dried in oven at 110 ºC for 24 h. For 10% Ni-dolomite catalyst, weight % was calculated on the metallic nickel and $Ni(NO_3)_2.6H_2O$ compound was used. Both dolomite and Ni/dolomite were used after calcination 5h at 850 ºC.

4.2. Methods

4.2.1. Experimental set up for pyrolysis

Pyrolysis experiments were carried out in vertical reactor which is a fixed bed design and of stainless steel with 60 mm diameter and 210 mm high. In a typical run, 100 g of GP or were placed into the reactor. The system was heated to the desired pyrolysis temperature at a heating rate of 5 ºC min^{-1}, and hold at this temperature for 1 hour. Two different pyrolysis temperatures, 300 ºC and 500 ºC were studied. One of the two thermocouples controls in the furnace temperature and the other controls the temperature inside the reactor. When carrying out the pyrolysis process as sweeping gas, nitrogen gas (25 mL min^{-1}) was passed through

the system. Experimental setup for pyrolysis is shown in Figure 4.1. End of the pyrolysis, the reactor was cooled to room temperature in a nitrogen gas stream and the char was taken.

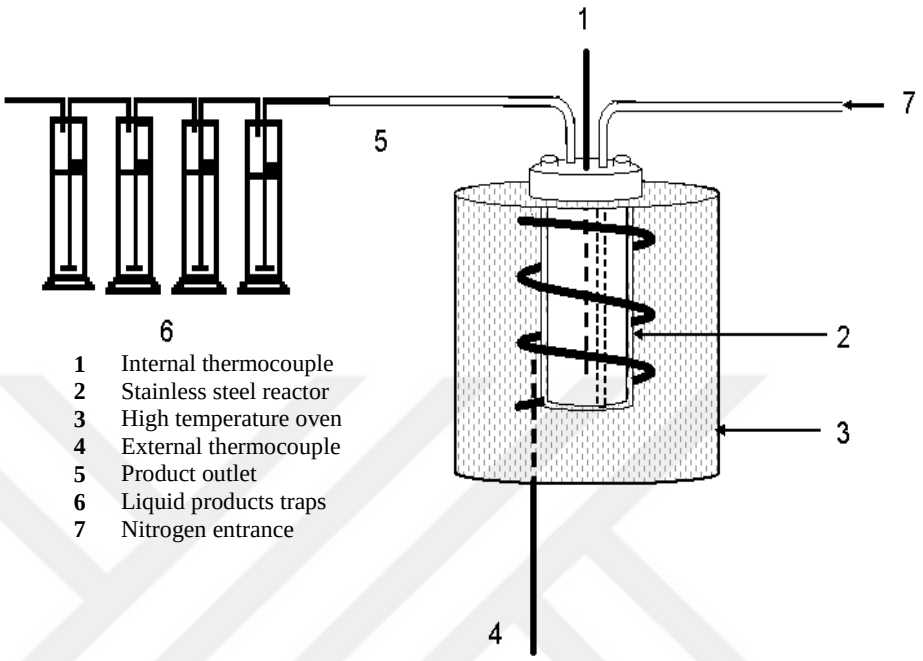

Figure 4.1 Pyrolysis reactor.

4.2.2. Experimental set up for gasification

Steam gasification of biomass or biochars was carried out in a vertical fixed dual bed semi-micro gasification reactor. A schematic diagram of the reactor system is shown in Figure 4.2. The top bed is for feedstock and the bottom bed is for catalyst. Approximately 1.0 g of feedstock which is placed in the top bed was gasified at 850 ºC in presence of H_2O-N_2 gas mixture. Steam flow rate was 0.07 g min^{-1} and 30 mL/min of flow rate for nitrogen. For the catalytic gasification experiments, catalyst (~ 3g) was placed in the bottom bed. After the bottom bed temperature reached at desired temperature (600, 700 and 850 ºC) biomass bed started to heat up to 850 ºC and hold at this temp for 20 min to complete the gasification of samples.

The gases were collected in two different stages first 200-400 ºC and 400-850 ºC. The evolved products from the reactor passed through and two dry ice cooled condensers where liquid products were collected.

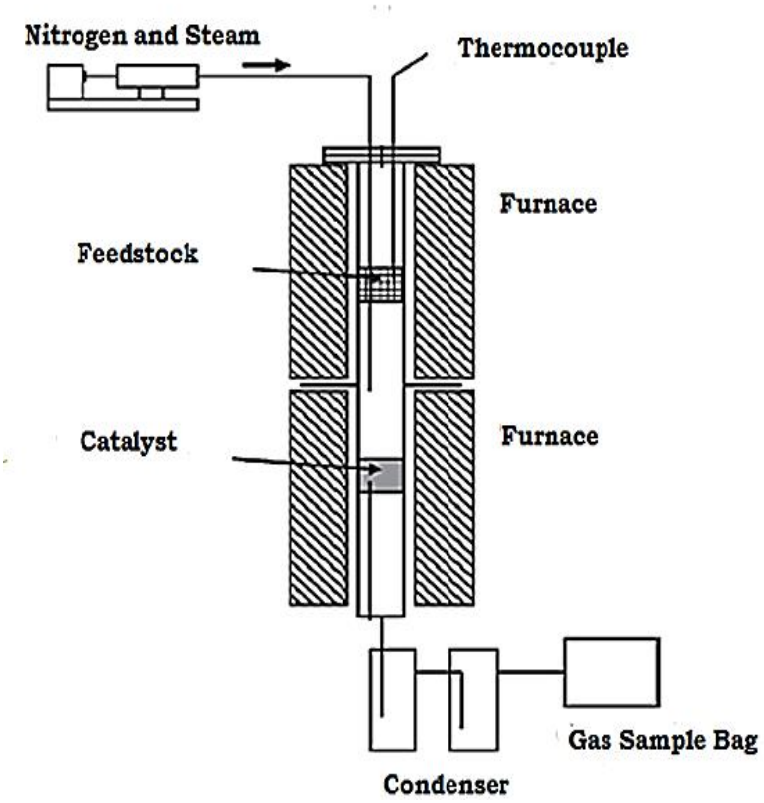

Figure 4.2 A schematic diagram of experimental system.

4.2.3. Analysis

4.2.3.1 Elemental analysis

C, H, N, and S contents of biomass and biochar were determined by using an elemental analyzer LECO CHNS 932 according to ASTM D5291-96. Oxygen amount was calculated by following equation.

O, % = 100 – (C % + H% + N% + S% + ash %).

4.2.3.2 SEM analysis

The surface morphologies and microstructures of the catalysts were investigated by scanning electron microscope (SEM) (JEOL-JSM 6060).

4.2.3.3 XRF analysis

The metal contents of the red mud and active red mud were analysed by the X-ray fluorescence technique.

4.2.3.4 Gas product analysis

Gas products were analyzed by RGA (Agilent Technologies 7890A GC System). This instrument is configured to analyze refinery gas within 13 minutes. The system has five valves and three detectors. The FID channel is configured to analyze the hydrocarbons from C1 to C5, while C6/C6+ components are back flushed and measured as one peak at the beginning of the analysis. The first TCD channel (reference gas He) is configured to analyze fixed gases, which may include CO_2, CO, O_2, and N_2. Last, the second TCD channel (third detector, on the side, with reference gas N_2) is dedicated to analyze hydrogen only.

5. RESULT AND DISCUSSIONS

In this study, steam gasification of different feedstock was investigated. Grape pomace, grape pomace char, lignite and blends of biomass/biochar: lignite (1:1) were used as feedstock. Gasification experiments were carried out at different bottom bed temperatures to investigate the effect of catalysts on both hydrogen and total gas yields. In all gasification experiments, the top bed temperature was kept at 850 ºC.

5.1. Biochar Yields

GP were pyrolyzed at two different temperatures (300 and 500 °C) in a fixed bed reactor. Approximately 62% and 34% char yields were obtained when the pyrolysis temperatures were at 300 ºC and 500 ºC, respectively. Char yield was decreased with increasing temperature. On the other hand, the ash and fixed carbon content and heating value of char were increased with increasing of pyrolysis temperature. The effect of pyrolysis temperature on char properties were given in Table 4.1.

5.2. Steam Gasification

5.2.1 Non-catalytic steam gasification

In our experimental system, the decomposition of biomass on top bed with steam proceeds in the following steps: pyrolysis of biomass and evolution of volatile matters including tars at 200–400 ºC; and steam gasification of char between 400 and 850 ºC in the top bed: Considering this two stages gas products were individually collected in two bags; at 200-400 and 400-850 ºC.

Table 5.1 shows the effect of bottom bed temperature on the yield and composition of the gas products evolved in the first stage (200-400 ºC). In this stage, the gas product consisted of both pyrolysis gases and gases obtained from tar decomposition.

Table 5.1 The gas yields from first stage gasification of biomass/biochar (top bed temperature: between 200 and 400 °C) at different bottom bed temperatures, mL gas/g feed.

Feedstock	**GP**			**GP300**			**GP500**		
Bottom bed temperature, ºC	600	700	850	600	700	850	600	700	850
HCs	0	<1	2	0	0	<1	0	0	0
CO	2	7	10	1	2	9	3	4	5
CO_2	0	0	0	0	<1	8	<1	2	3
H_2	1	3	7	<1	<1	8	<1	2	3
Total	2	11	20	2	2	19	3	7	8

As seen from Table 5.1, very low amount of gas product was obtained during first stage of gasification and temperature had no considerable effect on tar decomposition.

Table 5.2 The gas yields from second stage gasification of biomass/biochar (top bed temperature: between 400 and 850 °C) at different bottom bed temperatures, mL gas/g feed.

Feedstock	**GP**			**GP300**			**GP500**		
Bottom bed temperature, ºC	600	700	850	600	700	850	600	700	850
HCs	33	85	99	43	83	83	19	19	20
CO_2	371	487	537	509	518	557	623	629	675
CO	98	114	132	135	227	159	225	237	221
H_2	762	1005	1050	1196	1293	1306	1568	1570	1675
Total	1264	1691	1818	1884	2121	2105	2432	2455	2592

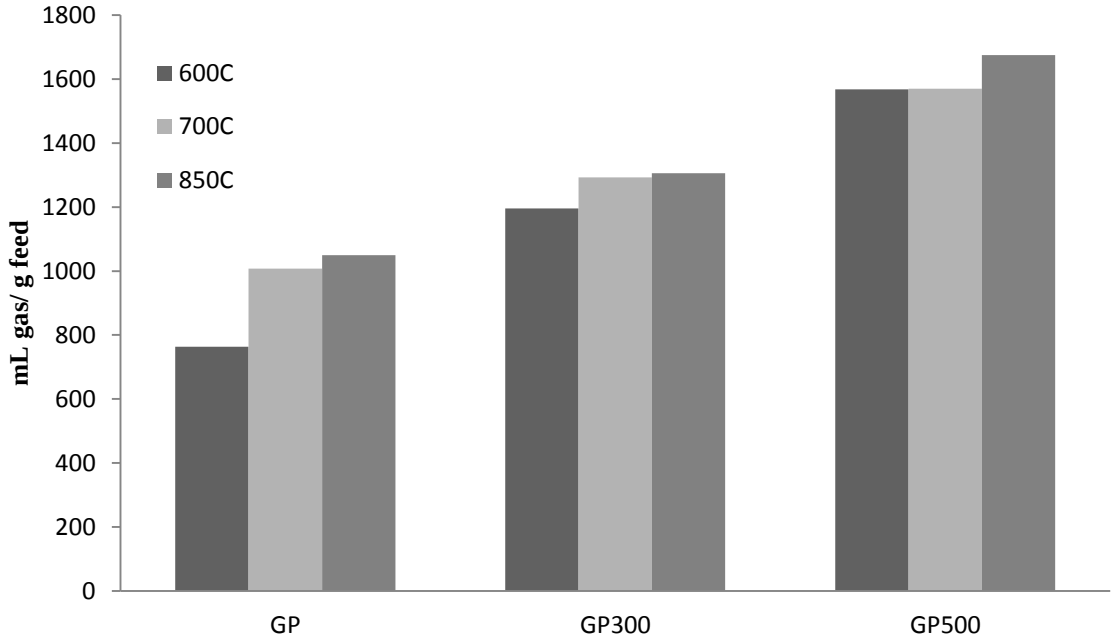

Figure 5.1 Total hydrogen gas yields of GP, GP300, and GP500 at different bottom bed temperatures.

As seen from Table 5.2, main gas production occurred during gasification between 400 and 850 ºC in top bed because of steam reforming of char. In case of GP, the bottom bed temperature had considerable effect on total hydrogen gas yield (Figure 5.1). However, there was generally a little increase in the amount of hydrogen from GP300 and GP500 as bottom bed temperature rose from 600 to 850 ºC. It is also seen in Figure 5.1, the yield of hydrogen from GP500 gasification was higher than those from GP and GP300 gasification for all temperatures. The reason was catalytic effect of alkali metals in the ash because GP500 had more ash content besides it had high carbon content.

In case of lignite gasification, we obtained very small amount of gas products in the first stage (Table 5.3), as in gasification of biomass and biochar. This shows that the volatiles, which formed from lignite pyrolysis between 200-400ºC, did not react with steam on the bottom bed at temperatures of 600, 700 and 850 ºC. For the second stage, high amount of gas product was produced. The highest hydrogen yield was obtained when bottom bed temperature was 850 ºC. During the gasification of lignite on top bed at the temperatures between 400-850ºC, the evolved products were gases formed from char gasification and tar. And these evolved products further may react with steam on the bottom bed. The

results in Table 5.3 shows that the products formed top bed reacted with steam on the bottom bed at temperature 850 ºC. By comparing the results in Table 5.3 with the results in Table 5.2, it can be seen that hydrogen yields from lignite gasification was much lower than that from biomass and biochar gasification. This reason may be that lignite has low carbon and low alkali metal contents.

Table 5.3 The gas yields of lignite gasification, mL gas/g lignite.

	first gasification step (200-400ºC)			second gasification step (400-850ºC)		
Bottom bed temperature, ºC	600	750	850	600	750	850
HCs	<1	<1	<1	37	40	48
CO_2	6	14	4	318	325	370
CO	0	1	<1	75	67	80
H_2	3	16	2	726	738	850
Total	9	31	5	1154	1171	1348

Co-gasification of lignite with biomass/biochar may be an alternative way to reduce negative environmental impact of utilization for lignite.

Gasification experiments of different blends containing lignite-GP, lignite-GP300 and lignite-GP500 were carried out to investigate synergic effect of biomass/biochar on coal gasification. The ratio of lignite in blend was 50 %. The hydrogen yields obtained from co-gasification were much more than that from lignite gasification (Figure 5.2). As in the gasification of lignite, GP and GP char alone, highest hydrogen yields were obtained from co-gasification when the bottom bed temperature was 850 ºC.

Table 5.4 The gas yields from first stage gasification of blends (top bed temperature: between 200 and 400 °C) at different bottom bed temperatures, mL gas/g feed.

Feedstock	**Lignite-GP**			**Lignite-GP300**			**Lignite-GP500**		
Bottom bed temperature, °C	600	700	850	600	700	850	600	700	850
HCs	0	0	1	0	<1	<1	0	<1	<1
CO_2	<1	2	23	1	26	26	6	11	26
CO	0	0	8	0	6	6	<1	1	4
H_2	<1	1	36	<1	38	39	7	3	33
Total	1	3	69	1	71	72	14	15	64

Table 5.5 The gas yields from second stage gasification of blends (top bed temperature: between 400 and 850 °C) at different bottom bed temperatures, mL gas/g feed.

	Lignite-GP			**Lignite-GP300**			**Lignite-GP500**		
Bottom bed temperature, °C	600	700	850	600	700	850	600	700	850
HCs	34	59	72	49	59	83	29	32	37
CO_2	201	217	437	398	447	531	515	550	575
CO	70	98	150	134	135	177	215	204	215
H_2	412	477	1042	943	1053	1288	1284	1345	1405
Total	718	858	1701	1524	1694	2079	2042	2131	2233

To see the synergic effects in co-gasification, theoretical yields were calculated. The theoretical and experimental results of hydrogen yields for co-gasification at different bottom bed temperatures (600, 700 and 850 °C) were given in Fig. 5.4. Positive synergy effect was observed with addition of biomass or biochar into lignite, except lignite and grape pomace blends when the bottom bed temperatures were 600 and 700 °C. In case of lignite-GP blend, anti-synergy effect was observed.

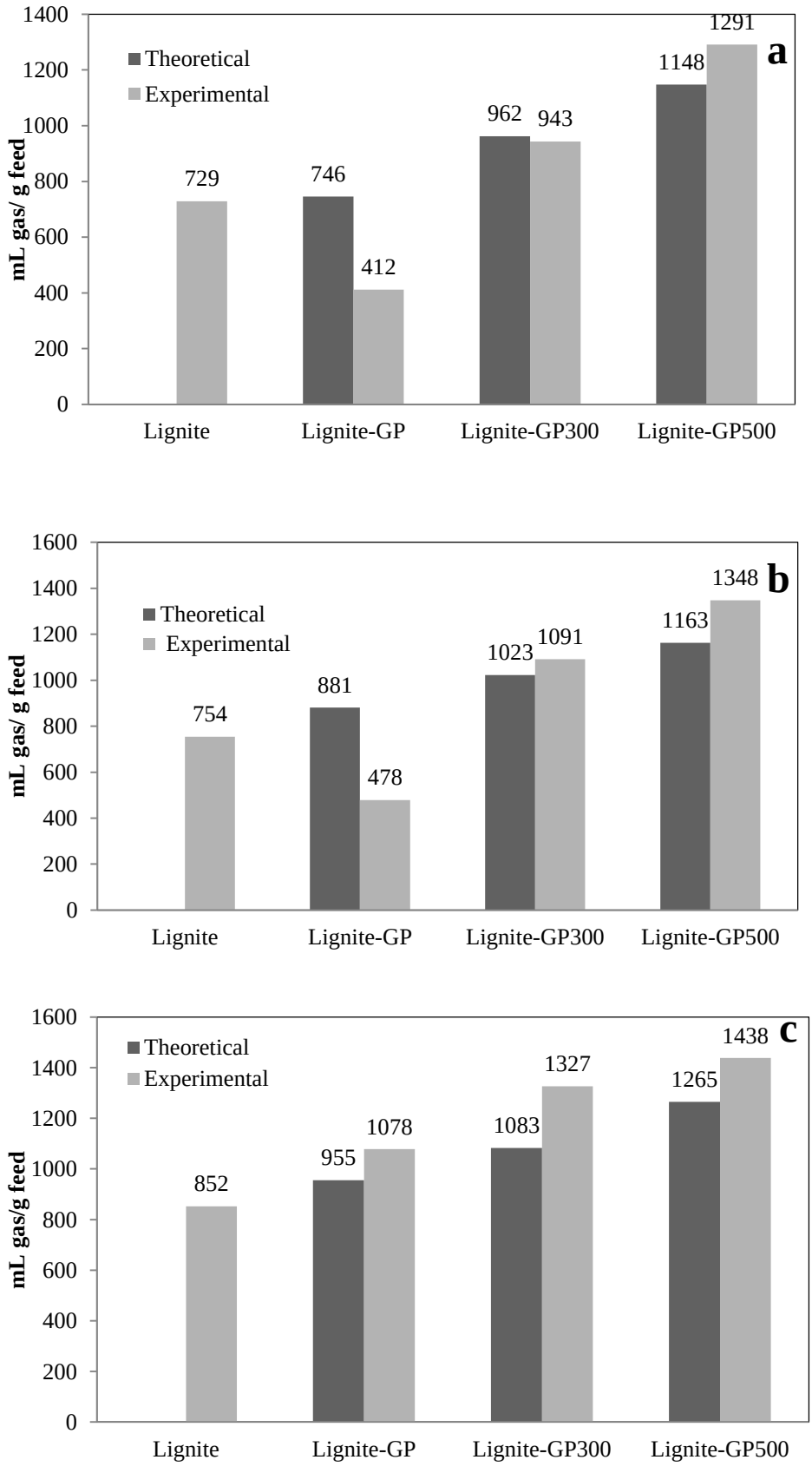

Figure 5.2 Comparison of theoretical and experimental total hydrogen yields for gasification of blends at bottom bed temperatures: (a) 600 ^{o}C, (b) 700 ^{o}C, (c) 850 ^{o}C.

Howaniec et al. (2014) were also reported the synergy effects in co-gasification of coal and biomass, increasing in the total gas and hydrogen yields. A correlation between ash composition (metal oxides contents) and synergy was noticed.

Ding et al. (2014) also studied the co-gasification of coal char and corn stalk char to investigate the interactions between them. They observed synergy effect in terms of gasification reactivity due to the high potassium content of biomass char.

5.2.2. Catalytic steam gasification

The effect of different catalysts on the gasification of biomass and biochar were investigated by the temperature programmed steam gasification of biomass in the top bed at 850 ºC followed by the catalytic gasification in the bottom bed at 850 ºC. The red mud, dolomite and 10% Ni-dolomite were used as catalyst. Figure 5.4 shows the gas yields from catalytic gasification in presence of red mud. For comparison, the gas yields from non-catalytic gasification of biomass. As seen Figure 5.3, red mud showed no catalytic effect on the gas yields in gasification of GP.

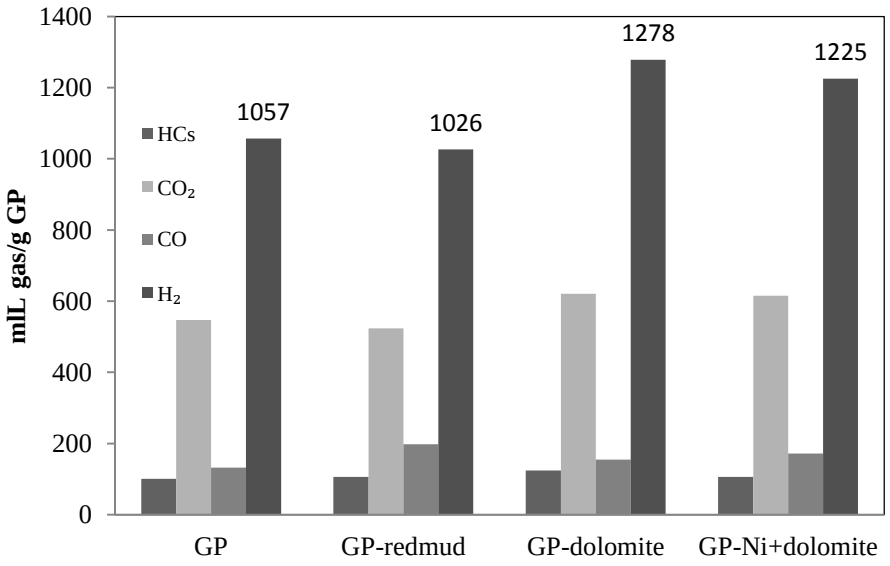

Figure 5.3 The total gas yields from thermal and catalytic gasification with red-mud, dolomite, 10% Ni-dolomite of GP.

In contrast to red mud, both dolomite and 10% Ni-dolomite catalysts led to an increase in hydrogen yields (Figure 5.3). Although Ni is well known a reforming catalyst, here Ni-dolomite showed similar activity with dolomite. The reason was the fact that volatiles from gasification would be a poison for Ni. Similar results were also obtained by Waheed et al. (2015).

Since red-mud showed no catalytic effect in gasification of GP, it was not used in further experiments. The catalytic gasification of GP300 was studied in the presence of dolomite and Ni-dolomite catalysts. In contrast to gasification of GP, Ni-dolomite was found more effective than dolomite in hydrogen production from GP300. Since some of volatiles were released during pyrolysis of GP, GP300 contained less amount volatile matter which caused poison of Ni in gasification. Because of this hydrogen yields in the presence of Ni-dolomite was more than that in dolomite (Figure 5.4).

Highest hydrogen yields were obtained from catalytic gasification of GP500. The catalysts used significantly increased the hydrogen yields.

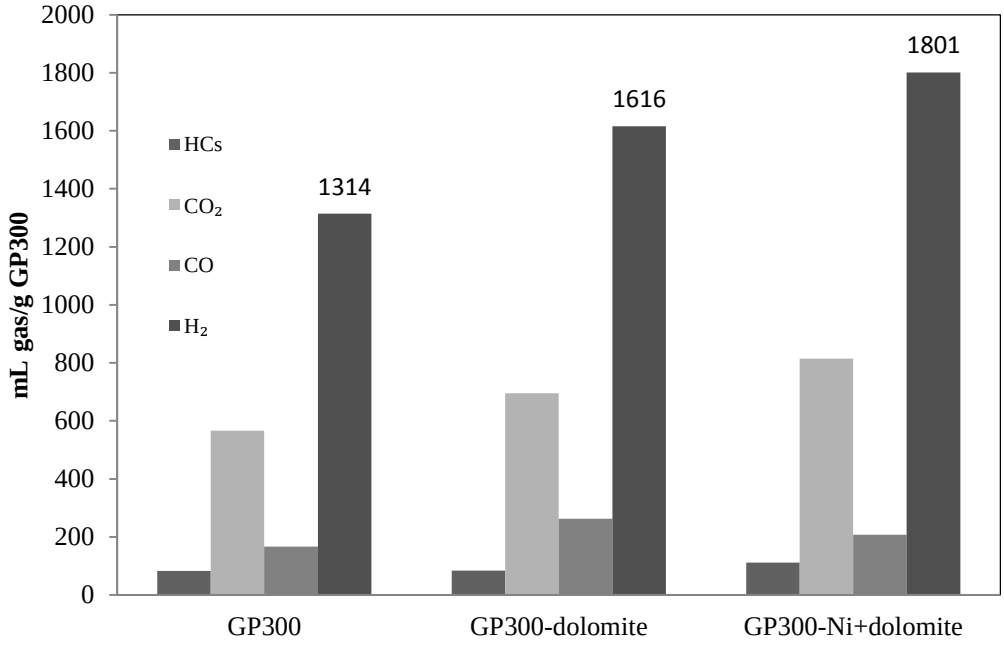

Figure 5.4 The total gas yields from thermal and catalytic gasification with dolomite, 10% Ni-dolomite of GP300.

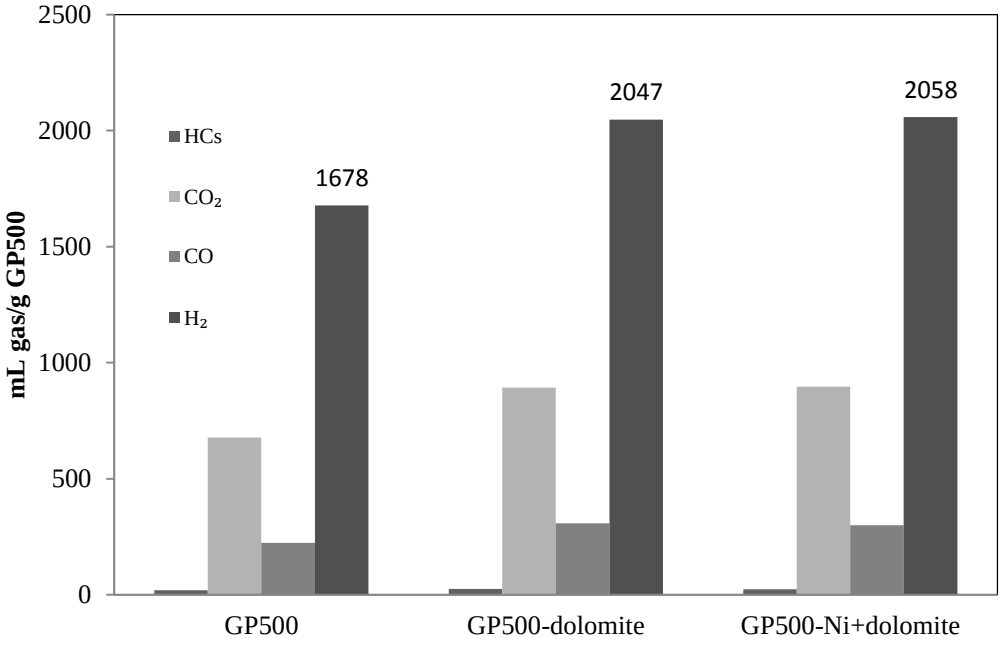

Figure 5.5 The total gas yields from thermal and catalytic gasification with dolomite, 10% Ni-dolomite of GP500.

5.3 SEM images of fresh and spent catalyst

To understand the change of surface properties of catalysts after gasification, we compared with SEM images of fresh and spent catalyst (Figure 5.6). It is interestingly that dolomite had porous character after gasification. The reason might be that hydration of dolomite with steam at the catalytic bed temperature of 850 ºC, leading to pore formation. The fact that the hydration of CaO improved morphology of the CaO was already reported in literature (Phalak et al. 2012).

On the other hand, for 10% Ni-dolomite, catalyst surface was coated with coke after gasification. This is reasonable because Ni promoted coke formation as well as reforming reaction.

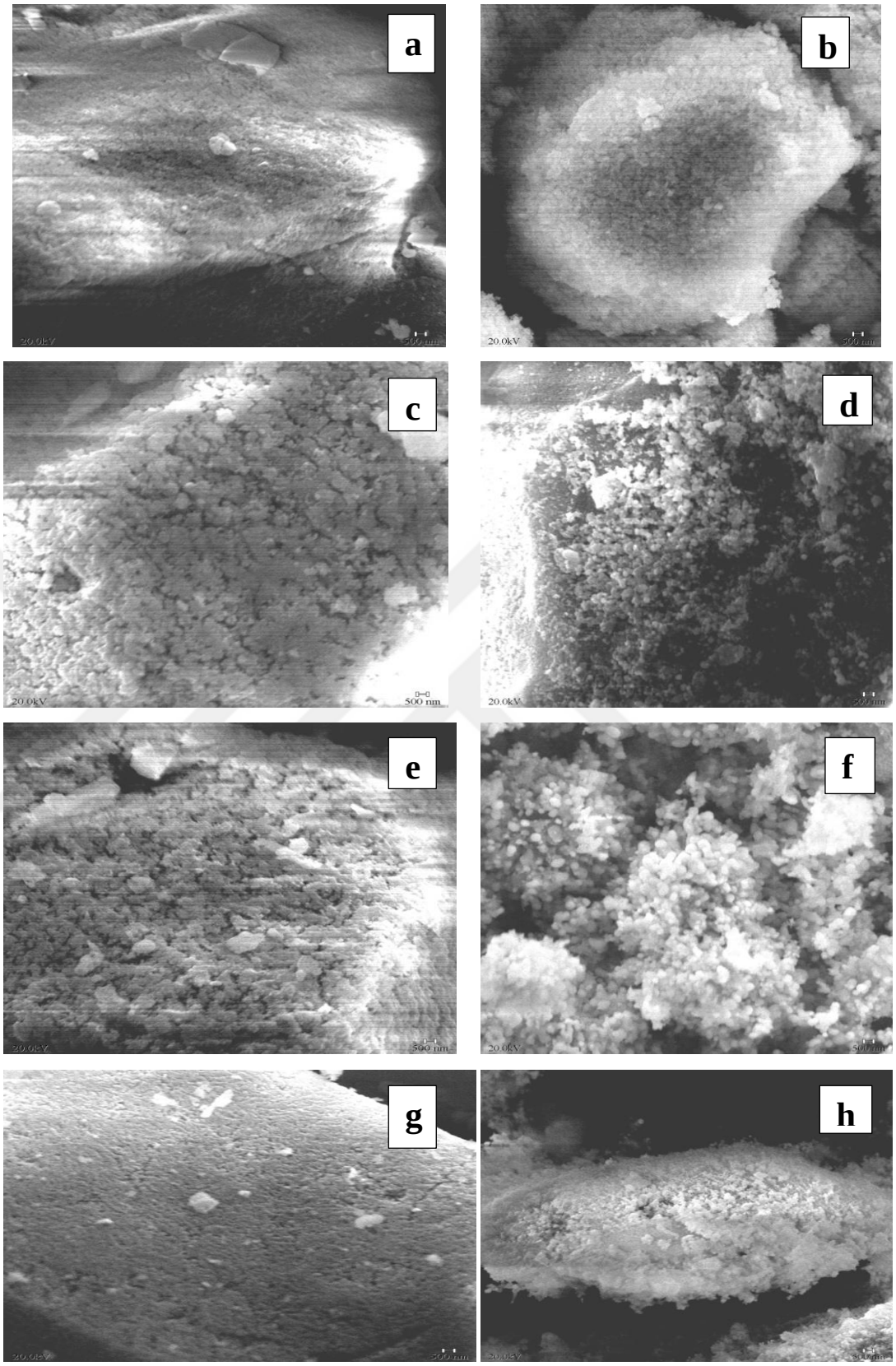

Figure 5.6 SEM results of the fresh catalyst and the reacted catalysts used with different feedstocks; a)fresh dolomite, b)fresh 10% Ni-dolomite, c) used dolomite with GP, d) used 10%Nidolomite GP, e) used dolomite with GP300, f) used 10% Ni-dolomite with GP300, g) used dolomite with GP500, h) used 10% Ni-dolomite (Magnification: 4000x).

6. CONCLUSION

In this thesis, catalytic and thermal gasification of grape pomace (GP), chars (GP300 and GP500) obtained from grape pomace and lignite alone and their mixture were carried out to produce hydrogen. The steam/nitrogen mixture was used as gasifying agent. Gasification experiments were performed in a vertical dual-bed reactor. The red mud, dolomite and 10% Ni-dolomite were used as catalyst. The effects of the catalyst type and the temperature of bottom bed on hydrogen gas yield were investigated. In addition, synergetic effect in thermal gasification of lignite /grape pomace (or chars) was investigated.

In thermal runs, hydrogen yield increased by increasing of bottom bed temperature from 600 ºC to 850 ºC, especially in the case of GP. The highest hydrogen yields obtained from thermal gasification were 1675 mL gas/g GP500, 1306 mL gas/g GP300 and 1050 mL gas/g GP. On the other hand, thermal gasification of lignite yielded a hydrogen gas of 852 mL gas/g lignite. In co-gasification experiments, positive synergic effect was observed with addition of biomass or biochar into lignite.

The use of dolomite and Ni-dolomite hydrogen yields considerable increased, whereas red mud had no catalytic effect. Ni-dolomite showed similar activity with dolomite. The highest hydrogen yields obtained from catalytic gasification were 2058 mL gas/g GP500, 1800 mL gas/g GP300 and 1278 mL gas/g GP.

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