INVESTIGATION OF TURKISH LIGNITES AND BIOMASS AT HIGH HEATING RATES BY USING WIRE MESH APPARATUS

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INVESTIGATION OF TURKISH LIGNITES AND BIOMASS AT HIGH HEATING RATES BY USING WIRE MESH APPARATUS

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

INVESTIGATION OF TURKISH LIGNITES AND BIOMASS AT HIGH HEATING RATES BY USING WIRE MESH APPARATUS

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Coal continues to play a significant role in energy production over the world. However, its limited procurement and enormous side effects on global warming, make governments and organizations turn towards renewable energy resources like biomass which is CO_2 neutral. Prior to utilization of fuels in power plants, it is important to investigate fuel behavior at high temperatures and high heating rates, i.e., close to heating rates in industrial applications. This understanding enables engineers to design appropriate and efficient boilers. However, until now, Turkish fuels have not been analyzed under high heating rate and high temperature conditions in laboratory settings to resemble the actual pulverized fuel combustion boilers. Therefore, in this study, combustion behavior of Turkish lignite and biomass fuels were studied in a laboratory environment close to the real conditions available in commercial power plants (i.e. pulverized fuel boilers). This work performed combustion and fast pyrolysis of Turkish biomass and lignite fuels, namely hazelnut shell (HS), olive residue (OR) and Soma lignite (SL) at high heating rates (~3000 ºC/s) in a novel wire mesh reactor (WMR). Particular emphasis was given to understand ash and char yields, their morphology and chemical composition, volatile yield, char reactivity of the chars obtained at high heating rates (~2200 ºC/s, 4550 ºC/s) and at elevated temperatures (~1100 ºC, 1500 ºC). In order to understand effect of moisture on fast pyrolysis conditions, dried and as received hazelnut shell fuels were pyrolyzed at two different temperatures, 1100 ºC and 1550 ºC, at heating rates of 2200 ºC/s and 4550 ºC/s respectively. Volatile yields from dried and as received HS chars obtained from both pyrolysis conditions, showed higher values nearly 85 wt.% than proximate analysis (PA) (HS-A: 75 wt. %, HS-D: 79.5 wt.%) performed at low heating rates (20 ºC/min). To investigate synergetic effect of co-pyrolysis of coal and biomass, two different blends of Soma lignite (SL) and hazelnut shell (HS) with mixing ratios of 50-50 wt.% and 75-25 wt.% were pyrolyzed. Thermogravimetric analysis (TGA) was conducted to carry out isothermal char combustion to study reactivity of individual and blended chars. In order to have kinetically controlled combustion environment in TGA, 400 º C for biomass chars, 450 º C for lignite and blended chars were decided as isothermal combustion temperatures. Individual hazelnut shell chars showed higher reactivity than individual lignite and blended chars and, therefore, shorter 90% burnout time (9.6 min) was observed for hazelnut shell chars compared to lignite (342 min) and blended chars (~160 min). Brunauer–Emmitt–Teller (BET) surface analysis was performed to determine surface areas of individual and blended chars obtained from high heating rate pyrolysis in WMR. Biomass chars were characterized by low surface areas (10-15 m^2/g) due to rapid volatilization phenomenon at high heating rates.

Keywords: Wire mesh reactor (WMR), Fast pyrolysis, High heating rates, Hazelnut Shell, Soma Lignite

ÖZ

INVESTIGATION OF TURKISH LIGNITES AND BIOMASS AT HIGH HEATING RATES BY USING WIRE MESH APPARATUS

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Kömür, dünyadaki enerji üretiminde önemli rol oynamaya devam etmektedir. Fakat, kısıtlı temin ve küresel ısınma üzerindeki büyük etkiler devletleri ve kuruluşları biyokütle (CO_2 nötr) gibi yenilenebilir enerji kaynaklarına yönlendirmiştir. Termik santralde yakıtın kullanımından önce, yakıtın endüstriyel uygulamalardaki yüksek sıcaklık ve ısıtma hızına yakın değerlerde yanma davranışını incelemek önemlidir. Bu tür bilgiler, mühendislerin daha uygun ve verimli kazanlar tasarlamasına olanak sağlamaktadır. Fakat, bu zamana kadar, Türk linyitleri ve biyokütleleri, laboratuvar ortamında pulverize yakıt kazanlarındaki koşullara yakın yüksek ısıtma hızı ve yüksek sıcaklıklarda çalışılmamış. Bu nedenle, bu çalışma kapsamında Türk linyiti ve biyokütle yakıtlarının yanma davranışı, mevcut termik santrallerdeki (ör. Pulverize yakıt kazanları) gerçek koşullara yakın şekilde olan laboratuvar ortamında çalışılmıştır. Bu çalışmada, fındık kabuğu (HS), zeytin tortusu (OR) ve Soma linyiti gibi Türk biyokütlesi ve linyitinin yeni geliştirilen tel örgü reaktöründe (WMR) yüksek ısıtma hızında (~3000 ºC/s) yanması ve pirolizi gerçekleştirilmiştir. Yüksek ısıtma hızlarında (~2200 ºC/s, 4550 ºC/s) ve yüksek sıcaklıklarda (~1100 ºC, 1500 ºC) oluşan kül ve çar miktarını, morfolojisini, kimyasal kompozisyonunu, uçucu madde miktarını ve çar reaktifliğini anlama hususuna önem verilmiştir. Hızlı piroliz durumunda nemin etkisini anlamak için kurutulmuş ve direkt alınmış fındık kabuğu yakıtının iki farklı sıcaklıkta (1100 ºC ve 1550 ºC) ve ısıtma hızlarında (2200 ºC/s ve 4550 ºC/s) pirolizi yapılmıştır. Kurutulmuş ve direkt alınmış fındık kabuğu (HS) yakıtının iki durumdaki pirolizinden çıkan uçucu madde miktarı düşük ısıtma hızında (20 ºC/dk) yapılan proksimat analizinden (HS-A: 75 ay. %, HS-D: 79.5 ay.%) daha yüksek değerler (%85 ay.%) göstermiştir. Kömür ve biyokütlenin birlikte pirolizinin sinerjistik etkisini incelemek amacıyla Soma linyiti (SL) ve fındık kabuğunun (HS) iki farklı karışımının (50-50 ay.% ve 75-25 ay.%) pirolizi yapılmıştır. Tek ve karışım halindeki çarların reaktifliğinin çalışılmasında izotermik çar yanması Termogravimetrik Analiz (TGA) ile gerçekleştirilmiştir. Termogravimetrik Analizde (TGA) kinetik olarak kontrol edilmiş bir ortama sahip olmak için biyokütle çarında 400 º C ve linyit ve biyokütle çarı karışımında 450 º C izotermik yanma sıcaklığı olarak kararlaştırılmıştır. Tek fındık kabuğu (HS) çarı, tek linyit ve karışım çarlarından daha yüksek reaktiflik göstermiştir. Bu nedenle tek fındık kabuğu (HS) çarının %90 yakıt tükenme zamanı (9.6 dk), tek linyit ve karışım çarları için gereken zamandan (sırasıyla 342 dk ve 160 dk) daha kısa olduğu gözlemlenmiştir. Yüksek ısıtma hızına sahip WMR pirolizinden elde edilen tek ve karışım çarların yüzey alanının bulunmasında Brunauer–Emmitt–Teller (BET) yüzey analizi gerçekleştirilmiştir. Biyokütle çarlarının, yüksek ısıtma hızında hızlı buharlaşma fenomeni nedeniyle düşük yüzey alanına (10-15 m^2/g) sahip oldukları gözlemlendi.

Anahtar kelimeler: Tel örgü reaktörü (WMR), Hızlı piroliz, Yüksek ısıtma hızı, Fındık kabuğu, Soma linyiti

To My Precious Family and Gorgeous Sweetheart

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TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Starting from industrial revolution, technology has been developing rapidly day by day which increases people's demand of energy. In order to supply this energy, non-renewable natural resources, such as, oil, coal, natural gas are widely being used. Significant amount of by-products, like CO_2, comes out from utilization of fossil fuels which causes a global warming and damages of ozone layer.

In order to inhibit global warming, governments and organizations are prone to use environmentally friendly, renewable energy resources such as, wind energy, solar energy, geothermal energy, hydroelectricity. Energy from biomass is also one of the renewable energy sources. Utilization of biomass in power plants in order to generate energy, can be carried out by co-firing of biomass with coal. Co-combustion of biomass and coal provides a marked reduction in CO_2 as compared to coal combustion.

According to the data provided by EPDK (Republic of Turkey Energy Market Regulatory) [1] shown in Fig. 1.1, in 2016 energy production of Turkey mainly came from utilization of fossil fuels, which was approximately 65 % of total share of energy supply (Natural Gas: 32 %, Coal: 33 %). As illustrated in Fig 1.1, coal sources that are used for energy generation in Turkey were mainly from indigenous lignite coal reserves (14.14 %) and from imported coal sources (17.52 %).

According to Republic of Tukey Ministry of Energy and Natural Resources, in 2017, biomass potential of Turkey was nearly 8.6 million tonnes of equivalent petrol (MTEP) [2]. Turkey has a wide variety of biomass sources, including olive residue, almond shell, hazelnut shell. Therefore, over recent decades governmental projects are focused on biomass technology.

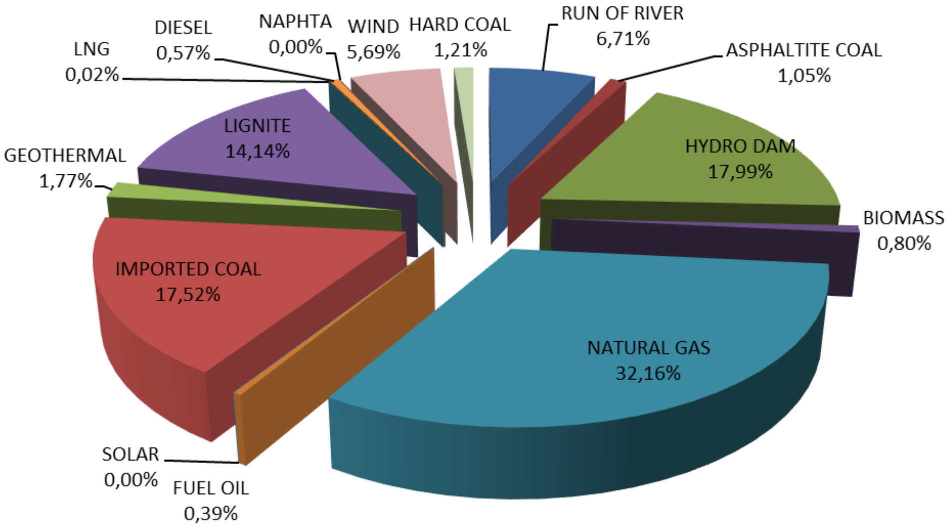

Figure 1.1 Energy generation by source in Turkey in 2016 [1]

Based on the data provided by Turkish Grain Broad [3], between 2012 and 2016, the average annual production rate of hazelnut in Turkey was 537,400 metric tons, which also comprised 67% of the global average annual hazelnut production. Therefore, in Turkey, hazelnut shell can be used as a major biomass source to obtain a clean energy. Hazelnut has a high heating value of approximately 19,300 kJ/kg found by the experiments and also calculated by equation (1) as presented by Demirbaş [4]

$$\mathrm{HHV} = \{33.5[\mathrm{C}] + 142.3[\mathrm{H}] - 15.4[\mathrm{O}] - 14.5[\mathrm{N}]\} * 10^{-2} \qquad (1)$$

Prior to utilization of coal and biomass fuels in power plants, fuel characterization is a crucial step in order to get idea about the fuel efficiency, fuel behavior at high temperatures and high heating rates. Characterization of fuels in terms of the ash/char yield, ash and char morphology and their chemical composition, enables engineers to design the most suitable and high efficient boilers.

There are various experimental rigs to investigate combustion characteristics of biomass and coal such as, drop tube furnaces, flat-flame burners, fixed bed reactors, wire mesh apparatus. Since the fuels are going to be burned at elevated temperatures in power plants, conditions of the experiments that are going to be performed in laboratory environment starts to play an important role in understanding real behavior of the fuels.

In the lab scale environment, wire mesh reactor (WMR) allows to conduct experiments under controlled conditions at high heating rates (~4500 °C/s) which resembles full scale combustion power plants. In wire mesh set-up, wire mesh usually made of stainless steel or molybdenum, acts as a sample holder and heats the sample by utilization of a power source. In WMR, since range of controllable heating rates is large, both slow (~300 °C/s) and fast heating rate (~4500 °C/s) experiments can be performed. In wire mesh set-up, both combustion and pyrolysis experiments can be conducted using either single layer or single particle configurations. Combustion of single particle experiments can also be monitored by using high speed cameras as studied by Flower et al. (2009) [5] and Riaza et al. (2017) [6].

Low-cost set-up configuration of WMR, easy and fast operability have always attracted researchers' attention where the very first study of wire mesh experiments goes back to 1964 by Loison et al [7]. WMR provides a valuable information which enables engineers to understand and to improve commercial scale power plants during their preliminary design stage [8].

Therefore, all these facts motivated the utilization of WMR in this study. Moreover, biomass potential of Turkey makes it attractive to use them in co-firing applications with coal. Since it is significant to study the fuel thoroughly prior to its utilization in real power plants, fast, easy and cheap configuration of wire mesh set-up with close conditions to power plants, constitute motivation of the present work. Characterization of Turkish biomass (hazelnut shell, HS and olive residue, OR) and lignite (Soma lignite, SL) fuels in terms of ash/char morphology, ash/char chemical composition and char reactivity were performed in this study, by using lab scale apparatus, wire mesh reactor (WMR), under the conditions close to the ones being applied in commercial power plants.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass and Coal Structure, Composition and their Industrial Utilization

Biomass is an organic matter which comprises materials that were directly or indirectly derived from photosynthesis reactions of forestry crops and residues, municipal solid waste, animal residues, agricultural and industrial wastes [9] (Fig. 2.1). Since the biomass sources are sustainable, and since no net CO_2 increment is observed when they are burnt, energy obtained from biomass is considered to be renewable and green energy [10]. Furthermore, biomass sources are energetically attractive, environmentally friendly and contribute to reduction of NO_x, SO_x emissions.

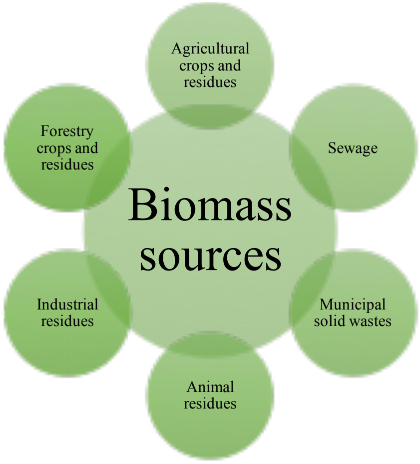

Figure 2.1 Biomass sources

Structure, chemical composition, type and origin of biomass has an effect on the whole thermal processes of biomass [11]. Biomass consists of three major structural organic components: lignin, cellulose and hemicellulose, where their corresponding percentages vary depending on type of biomass source [12].

Cellulose, an organic polymer, mainly contains anhydroglucose which is connected by β-(1,4)-glycosidic bonds as a long straight-chain molecule [13]. Contrary to cellulose, hemicelluloses which are amorphous short polymer chains, possess various monosaccharide elements and hold the cellulose micelles, fibers together [13]. The third structural element, lignin, which has a three-dimensional morphology, strengthens the system and hinders the degradation phenomenon in plants [13].

Biomass also constitutes a significant amount of inorganic matter which act as impurities and strongly depend on the origin of biomass [9]. Inorganic matter in solid fuels including in biomass are studied under two main category, inherent inorganic material and extraneous inorganic material [9]. Inherent inorganic materials mainly consist of inorganic salts, oxides, nitrates, sulphates, phosphates, chlorides, alkaline and earth alkaline metals, while extraneous organic materials come during harvesting, storage, and fuel processing [9].

Compared to coal, biomass has a different and wide range of chemical composition where in descending order it is rich in Mn, K, P, Cl, Ca, Mg, Na, O, moisture, volatile matter, and low in H, ash content, Al, C, Si, S, Fe, N, Ti.

As reported by Demirbaş [14], due to high volatile matter and high reactivity of biomass fuels, it is advantageous to utilize it in thermochemical processes. Nevertheless, it has more oxygen, low carbon and hence low heating value as compared to fossil fuels.

In order to extract the energy from biomass, various thermochemical processes are performed [15]. They are direct combustion, gasification, pyrolysis, hydrothermal processing and hydrolysis to sugars.

When the biomass is directly burned in combustion process, possible thermal energy with moderate and high temperature (800-1600 ºC) which is going to be obtained from the process, enables to generate electric power [15].

Fast pyrolysis which is also known as devolatilization, takes place at 450-550 ºC in an inert atmosphere and produces char, with a smaller amount of syngas, condensable vapor and aerosols [15]. At pressures between 50-250 atm and temperatures around 200-500 ºC, in order to hinder boiling of water in slurry, hydrothermal process takes place. It disintegrates the biomass into its major components, cellulose, hemicellulose and lignin [16].

Geographical location of Turkey allows it to have a wide variety of biomass sources. Due to widely spread agricultural activities in Turkey [17], forest and agricultural residues are commonly used as biomass sources to generate an electricity. Turkey is rich in olive, hazelnut, almond, walnut and some others. Therefore, shell, husk, stalk, bagasse are common residues obtained from oily seeds and are utilized as a biomass source in Turkey [17].

Hazelnut shell has an important role among biomass sources of Turkey. Table 2.1 from Demirbaş's study [18] shows the percentage of major structural components and ultimate analysis results of hazelnut shell obtained from Trabzon province.

Table 2.1 Structural (wt.% daf) and ultimate analysis (wt.& dry) Turkish hazelnut shell [18], [19].

	Hazelnut shell	Olive residue
Hemicelluloses (wt.% daf)	30.4	9.4
Cellulose (wt.% daf)	26.8	36.2
Lignin (wt.% daf)	42.9	54.3
Carbon (wt.% dry)	51.6	48.3
Hydrogen (wt.% dry)	6.2	6.2
Oxygen (wt.% dry)	40.2	44.7
Nitrogen (wt.% dry)	1.6	0.7
Sulphur (wt.% dry)	0.04	0.1
Ash (wt.% dry)	1.4	2.3
HHV (MJ/kg)	20.2	19

Another type of biomass which is found abundantly in Turkey is olive residue. It is a yield obtained from the process in which the main product is going to be olive oil. As reported by Yuzbasi et al. [20], top countries that produce the olive oil in the world are, Spain, Portugal, Italy, Greece, Turkey, Tunisia and Morocco. In Turkey, olive production showed increase from 1.2 million tons in 2000-2001 to 1.7 million tons in 2014-2015 [21]. Structural and ultimate analysis results for olive residue reported by Kazanç et al. [22] are shown in Table 2.1.

Coal is a heterogeneous rock which consists of macerals, minerals and inside submicron pores water and gases [23]. Macerals are known as organic matter which are formed from plant residues [23] and is found largely in coal, while minerals are inorganic part of the coal and are left as an ash at the end of the combustion processes. Organic and inorganic matter of coal play an important role during thermal processes of coal. Inorganic content of the coal may cause deposition of some matter over the reactor surfaces which consequently may reduce thermal efficiency and pose erosion or corrosion problems of structural parts of the reactor [24].

Based on carbon concentration, coals are categorized under four types which are, anthracite, bituminous, subbituminous and lignite (in descending order of C content).

Comparing low rank coals (lignites) to higher ranked ones, ash, volatile matter, moisture, H, N, O, S are abundant in low rank coals [25]. Ash content of low rank coals is high in MgO, SO_3, CaO while low in SiO_2, Al_2O_3 contrary to high rank coals [25]. However, high rank coals are rich in SiO_2, Al_2O_3, Na_2O, K_2O, Fe_2O_3, TiO_2 [25]. Among the mineral species, alumina silicate clay minerals in coal composition have a key effect in structural framework of coal [26].

Coal is a primary energy source for power generation in Turkey. Turkey is rich in lignite deposits which have high amount of moisture, sulphur and ash while low content of fixed carbon. Those lignites are Afşin-Elbistan, Orhaneli, Seyitömer, Tunçbilek, Soma, Kemerköy, Yeniköy and some others.

2.2 Biomass/Coal Combustion

Combustion is an exothermal chemical reaction of a fuel with oxygen, which releases CO_2 and water vapor together with by-products at the end of the process. Fuel, oxygen and sufficient heat are the three major things that are required to start and to sustain the combustion process.

When the solid particle is heated, combustion process starts with drying stage where the water content releases and then devolatilization stage takes place which is release of volatile matter from a fuel in the form of the gas. As released volatiles mix with oxygen combustion occurs. Drying and devolatilization stages start and finish in a very short time. After combustion of volatiles, solid fraction which is called char starts to burn and lasts relatively long as compared to burning of volatile matter. At the end of a solid fuel combustion process, solid inorganic matter yields which is called ash. This route is illustrated in Figure 2.2 adapted from reference [27].

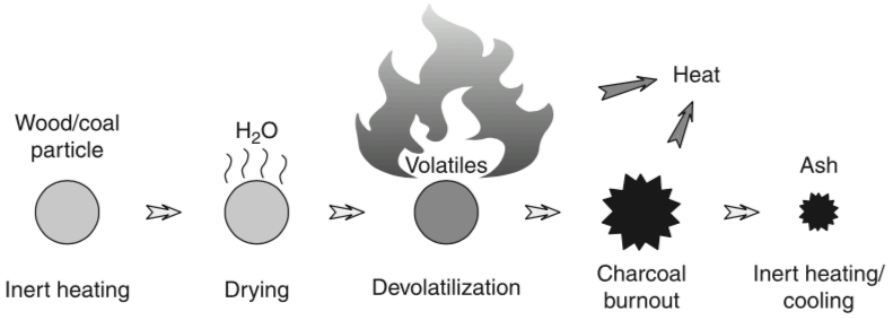

Figure 2.2 Combustion mechanism of a sloid fuel particle [27].

Biomass absorbs CO_2 from the atmosphere and energy from the sun where it stores this energy chemically via photosynthesis process [27]. When the biomass is burned, the stored energy and CO_2 are released to atmosphere. Therefore, biomass combustion is considered to be CO_2 neutral meaning that this process does not contribute to the increment of CO_2 emission in atmosphere.

Following is a global combustion reaction of hydrocarbon fuels as reported by Mando et al. [27], which states that combustion process converts the solid fuel into CO_2, water and heat.

$$C_{X_1}H_{X_2}O_{X_3}N_{X_4}S_{X_5} + n \cdot (3.76\ N_2 + O_2) \rightarrow aCO_2 + bH_2O + cO_2 + dN_2 + eCO + fNO_x + gSO_x$$

Origin of a solid fuel (coal, biomass), its chemical composition, harvesting, transportation, temperature and heating rate of a combustion process significantly affect combustion characteristics of a fuel. As reported by Mando et al. [27], there is a reverse relation between heating value and moisture content of the fuel. Heating value of the fuel decreases as moisture content increases, and in the case of moisture content more than 55 wt.%, it is hard to sustain a combustion [27]. Moreover, required residence time for a complete combustion of a fuel increases as water content in the fuel increase [27].

Burning low rank coal which has high content of sulphur or burning biomass which contains high amount of volatiles and alkali metals may have hazardous effects on boilers due to ash depositions on the tubes of the boiler [28]. Due to low melting temperature of biomass ash, fouling and slagging issues may arise [10]. Moreover, since biomass has low heating value compared to coal, flame instability problems may arise which can be solved by utilizing biomass together with high heating value fuels [10]. Therefore, nowadays, for power generation, co-firing of biomass and coal has become an attractive method for many countries which reduces net SO_x, NO_x and CO_2 emissions. To illustrate effect of co-firing on NO_x reduction, as discussed by Sami et al. [10], when HC reacts with NO_x, it produces N_2, hence, during co-combustion, HC coming from volatile matter will reduce NO_x to N_2. Therefore, according to Sami et al. [10], as volatile matter increases, more NO_x reduction will be observed [29].

Moreover, in co-combustion of coal and biomass, synergetic effect can be observed in terms of enhanced reactivity of chars, high yields of tar and better quality of pyrolysis products [30].

2.3 Biomass/Coal Pyrolysis

Pyrolysis is a very first stage of a solid fuel combustion. It is known as thermochemical decomposition of an organic matter in an inert atmosphere at high temperatures. In some studies, this phenomenon is also referred as devolatilization stage (see Fig. 2.3) [31]. In the lab environment, it can be performed in a vacuum condition or in a desired inert atmosphere such as Nitrogen or Helium.

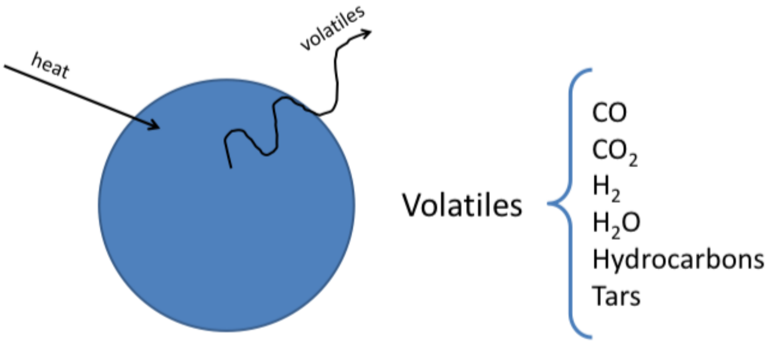

Figure 2.3 Solid fuel pyrolysis [31].

In pyrolysis of solid fuel, after vaporization of volatiles (CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6) and liquid yields (tars, heavier hydrocarbons, water), there is still left a remaining solid residue which consists of ash and fixed carbon and called as char [32]. Studying pyrolysis of solid fuel enables researchers to characterize fuel and to predict upcoming stages of solid fuel combustion.

Composition of a solid fuel, particle size, heating rate and pyrolysis temperature have a significant influence on pyrolysis products. Common gaseous yields from pyrolysis of woody biomass are, CO, CO_2, CH_4, H_2 and other organic compounds [10].

Char obtained from bituminous coal pyrolysis which has a low oxygen content may have graphitic morphology, while in biomass chars no such structure may be observed due to high hydrogen and oxygen content in biomass compared to coal [10]. Based on explanation done by Wornat et al. [33], due to structurally disordered nature of biomass chars, highly reactive edge carbons may present in the structure which will enable to have high reactive chars in the late steps of combustion process.

Heating rate is an important parameter affecting char yield concentration from solid fuel pyrolysis. There are several methods that are frequently used in lab scale environment to study solid fuel pyrolysis at low heating rates (5 K/min). One of them is thermogravimetric analyzer (TGA). Results of TGA are usually utilized as a reference data.

In order to conduct high heating rate (1000-10 000 ºC/s) pyrolysis experiments in lab scale, there exists several reactors, such as, Drop Tube Furnace (DTF), Wire Mesh Reactor (WMR). Results from these reactors are more realistic and close to the ones obtained from large scale power plants.

When the data from low (i.e. 20 ºC/min) and high heating rate (i.e. >1000 ºC/s) reactors are compared, a significant effect of heating rate on the yields can be observed. For example, pyrolysis of biomass at high heating rates and at high temperatures with low residence time, results in low amount of char yield with a high reactivity [34], [35], [36] . Moreover, enhanced devolatilization at elevated heating rates, may cause high volatile yields [35], which is not the case in low heating rate (20 ºC/min) and in 950 ºC proximate analysis, where implementation of secondary reactions of the tar diminishes final volatile yield [37]. High volatile yield may also be originated from gasification of char-CO_2 [22], [38], [39], [40] at high temperatures (~1300 ºC). Furthermore, pyrolysis at high heating rates (>10^3 ºC/s) may cause plasticization of char in which melting of the char structure is going to be observed [41].

To add more, during high heating rate pyrolysis fast release of large amount of volatiles causes crash of micropores which result in creation of macropores [42]. As a consequence, char surface areas may reduce.

2.4 Wire Mesh Reactor (WMR)

In recent years, wire mesh reactor has become a widely used experimental rig in order to study solid fuel pyrolysis and combustion. Motivation of using this set-up in the present work, is easiness of obtaining high heating rates, which resembles a real-life power plant environment. Rapid pyrolysis at elevated temperatures plays a key role as it happens during the first stages of combustion and gasification processes. Therefore, pyrolysis conditions significantly influence char yield and their reactivity [36].

One of the very first hot wire pyrolysis experiments was conducted by Schlutz et al. [43] in 1955. In hot wire set-up, authors studied decomposition rate of polymethylmethacrylate in an inert nitrogen atmosphere. Nichrome or Kanthal wires were heated by electric heater and temperature recordings were obtained by using thermocouple where it was welded to the top center of the hot wire.

Study performed by Cogliano et al. [44] in 1963 investigated pyrolysis of motor oil at a low residence time in a newly designed apparatus. In the reactor, sample was held in a petri dish and the coil coated with platinum was put in a dish. Power was supplied to the coil from the storage batteries. In contrast to the work done by Schlutz et al. [43] where the thermocouple was used to measure temperature measurement, Cogliano et al. [44] obtained temperature of a wire from a voltage drop. The apparatus designed by Cogliano et al. [44], was able to create heating rates of nearly 1000 K/s.

Loison et al. (1964) [7] was the first to propose the wire mesh to be utilized as a sample holder, and the mesh was heated by using alternating current as reported by [45].

A direct current reactor which was designed by Finch et al. (1969) [46], enabled authors to study properties of solids under very high heating rates, 165 000 ºC/s. Such high heating rates were provided from nickel-cadmium type storage batteries under 1000A-5000 A of currents. Connection between power sources and sample holder was done by using copper bars. Samples had to be in the dimensions of 0.3175 cm x 7.62

cm in order to be tested in the set-up. Appropriate optical window designed on the stainless-steel chamber for high speed camera imaging. Another optical window was provided on top of the chamber for the utilization of pyrometer.

Anthony et al. (1974) [47], investigated rapid reaction of pulverized coal with hydrogen under high heating rate (600 ºC/s -12000 ºC/s) conditions. A single layer of coal particles was placed on a 325 stainless steel screen which was heated electrically. Temperature measurement was obtained by placing thermocouple in between the screens. According to the authors' explanation, temperature of a thermocouple, screens and coal particles can be considered to be similar since the decrease of a temperature gradient between the stainless steel plates was very rapid.

Hamilton et al. (1979) [48], studied pyrolysis of coal under high heating rates (10000 C/s) and controlled conditions by utilizing stainless steel wire mesh as a sample holder. Contrary to Anthony et al. [47], for accurate temperature measurements, thermocouple was welded to the mesh. Pyrolysis experiments were performed both in nitrogen and in vacuum atmosphere. The work aimed to study char and gaseous yields obtained from pyrolysis of coal.

Drummond et al, (1996) [49], conducted pyrolysis experiments of sugar cane bagasse using wire mesh apparatus at different heating rates, 0.1 ºC/s, 1 ºC/s, 100 ºC/s and 1000 ºC/s and residence times, 0 s, 30 s, 100 s. During the pyrolysis experiments, liquid nitrogen was poured from top open part of the trap which swept the pyrolysis gases and had an effect on reduction of secondary reactions or possible polymerizations. Thermocouple in the diameter of 0.05 mm was used to measure temperature of wire mesh. At the end of experimental trials, char yields and tar yields were investigated.

Flower et al. (2009) [5], performed a single biomass particle combustion tests by using wire mesh apparatus. In their study, meshes were placed vertically and in between them K type thermocouple in 1 mm of diameter and a particle holder with two parallel wires were placed. During the experiments, particle was heated by thermal radiation. Due to small particle size, it was hard to measure temperature of the particle by using either thermocouple or pyrometer, and therefore K type thermocouple was placed to be sure if a generated heat flux during the trials were consistent with each other or not. This study conducted a different type of temperature measurement technique which was measuring resistance of a mesh. In order to monitor biomass particle ignition, high speed camera was utilized.

Di Nola et al. [50] studied fast pyrolysis of coal and biomass fuel samples using wire mesh reactor in 2009. At the same time in-situ gas analysis was performed by using FTIR spectrophotometer. Pyrolysis experiments were performed under inert Helium atmosphere. Temperature measurement was conducted by using 200 μm diameter S type thermocouple (Pt/Pt-Rh) which had a contact with the mesh. In this study, there were two chambers namely reaction and measuring chambers. In the first chamber, pyrolysis experiments were conducted, and when the gaseous products were released due to circulation pump, products were mixed much more uniformly and collected at measuring chamber where the FTIR analysis was performed. Effect of temperature, high heating rate and residence time on pyrolysis yields were investigated.

In the work carried out by Prins et al. [51] in 2009, pyrolysis of biomass at 1000 K/s heating rate conditions in wire mesh reactor was performed. Through optical window, imaging was conducted by using high speed infrared camera. Similar to previous studies, temperature measurements were obtained by utilizing thermocouple. According to Prins et al. [51], in wire mesh reactor there is a minimum weight loss of a fuel in the stage of heating which is advantageous compared to TGA (thermogravimetric analysis). Hence, such minimum weight loss prevents possible changes in reactivity of a fuel that can happen while temperature reaches to the final pyrolysis temperature [51]. In this study, K type thermocouple was used to get temperature information of the mesh. Wire mesh was heated through the electrodes where the current was supplied to the electrodes from the power source.

Trubetskaya et al. (2015) [35] conducted a pyrolysis study of pinewood, beechwood and wheat straw in a single layer wire mesh arrangement to understand effect of temperature and high heating rates on char yields. In the set-up, wire meshes were bended from the sides in the form of bag to prevent loss of fuel during experiments. Set-up was appropriate to carry out experiments up to 1700 °C temperatures with heating rates up to 5000 °C/s. Heating rates of 10 °C/s – 600 °C/s was the range where the marked effect of increase of heating rate was detected. Due to large heat flux and more uniform temperature, smaller particles were converted faster. However, larger particles had internal temperature gradients and thus lower heat flux was observed which led to a slower pyrolysis. Changes in morphological structures of the chars obtained from high heating rates were observed. Due to high heating rates, macroporous and melt like chars were obtained.

Zhang et al. (2017) [52], studied fast pyrolysis of biomass in a much-developed wire mesh reactor. Stainless steel (SS 304) wire meshes were clamped in between the electrodes and were heated through electrodes by using current connector. As in Trubetskaya et al. (2015) [35], samples were placed in between of a folded mesh in order to prevent loss of fuel particles during the pyrolysis. Steering flow was applied to sweep the pyrolysis gases out of the reactor and to prevent their deposition over the mesh. In the set-up, there was concentric quartz tubes in order to collect and weight the tar yield. One of the electrodes was connected to a spring in order to control single layer particle distribution over the mesh. Experiments were conducted under different heating rates, 5 °C/s, 40 °C/s, 250 °C/s, 1000 °C/s and the results were compared with the ones obtained from low heating rate TGA analyses.

Above mentioned apparatus, wire mesh reactor, has not been utilized to study Turkish fuels at high heating rate and high temperature conditions in the literature. In this work, wire mesh reactor (WMR) was used to investigate combustion and fast pyrolysis of Turkish fuels and their blends at high heating rates (~3000 ºC/s) for the first time in the literature. Ash and char yields, their morphology, chemical compositions and char reactivities were studied in this work which will shed light into the combustion characteristics of the Turkish fuels in pulverized combustion system.

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODOLOGY

This chapter describes sample preparation steps, methodologies and materials that were used to conduct combustion and pyrolysis experiments. Experimental conditions and the parameters which were chosen to study their effects on the fuel yields were also outlined in this section. Novel wire mesh reactor (WMR), other experimental apparatuses such as ashing furnace, thermogravimetric analayzer and experimental techniques like scanning electron microscopy (SEM), BET surface area analysis which were performed to investigate the morphology of the yields from combustion and pyrolysis of the fuels were elaborated in the following subsections.

3.1 Fuels and Fuel Preparation

In this study, Turkish biomass and coal samples were characterized in combustion and pyrolysis experiments. Hazelnut shell (HS) and olive residue (OR) were used as biomass sources, and Soma lignite (SL) was used as a coal source. Hazelnut shell and Olive residue which are abundant industrial and agricultural residues in Turkey, were obtained from Trabzon and Havran-Balıkesir provinces respectively. Soma lignite which is one of the main coal sources in Turkey for electricity generation, was supplied from mining region of Soma-Manisa.

At Mineral Processing Laboratory of Mining Engineering Department at Middle East Technical University, biomass and lignite fuel samples were crushed by using roll crusher and ring mill consecutively. Then, fuel preparation process was followed by sieving crushed fuels to particle size range of 106-125 µm by using ASTM (American Society for Testing and Materials) standard sieves at Clean Combustion Technologies Laboratory of Mechanical Engineering Department at Middle East

Technical University (Figure 3.1). Ultimate analyses of the samples (Table 3.1) were carried out by elemental analyzer at Thermal Analysis Laboratory at Central Lab at METU. Proximate analyses of biomass and lignite samples were performed by using thermogravimetric analyzer (TGA) at Department of Aerospace Engineering at METU. During the proximate analysis, the samples 1) were heated up from room temperature to 120 °C with 50 °C/min in nitrogen environment, then 2) the samples were held at 120 °C for 3 min, 3) after that, the samples were heated up to 950 °C with 100 °C/min, 4) then they were cooled down to 450 °C with 100 °C/min and then 5) air was switched and 6) heating up of the samples to 800 °C with 100 °C/min was performed where 7) they were held at 800 °C for 3 min as reported by Garcia et al. [53]. Afterwards, for pyrolysis experiments of biomass and lignite blends, two different mixing ratios, 50% SL – 50% HS and 75% SL – 25% HS were prepared mechanically and pyrolysed to study effect of blends in co-pyrolysis.

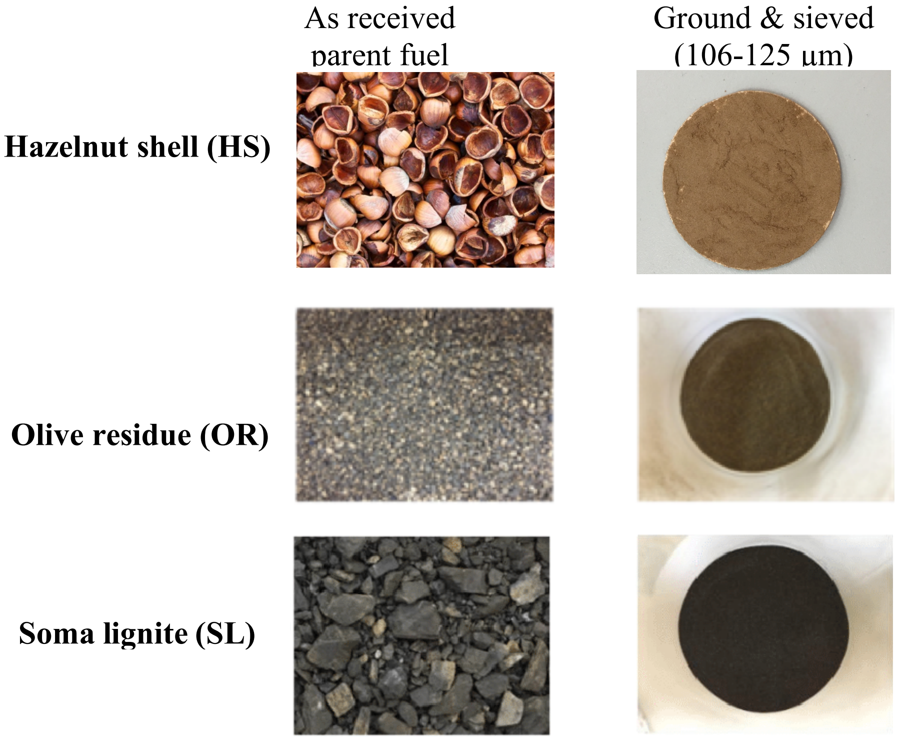

Figure 3.1 As received and grinded biomass and coal samples.

Moisture effect of as received hazelnut shell (HS) which was 5.5 wt. % (see Table 1) was investigated in pyrolysis experiments. Therefore, HS fuels (as received) were left overnight in the furnace at 150 °C to dry. Then, both as received and dried hazelnut shell (HS-A and HS-D respectively) samples were pyrolysed at high heating rates (2200 °C/s and 4500 °C/s) at wire mesh reactor (WMR).

To be able to conduct combustion and pyrolysis experiments at wire mesh reactor (WMR), 1) two wire meshes were cut into sizes with an area of 75x40 mm, and 2) biomass/coal samples were placed to the middle section (elaborated in section 3.2.1) of the mesh in a single layer, then 3) the meshes was put on top of each other. In order to prevent loss of particles during combustion or pyrolysis experiments, meshes were folded from the sides. Figure 3.2 shows the preparation procedure of hazelnut shell combustion/pyrolysis experiment with stainless steel (SS 316) wire mesh.

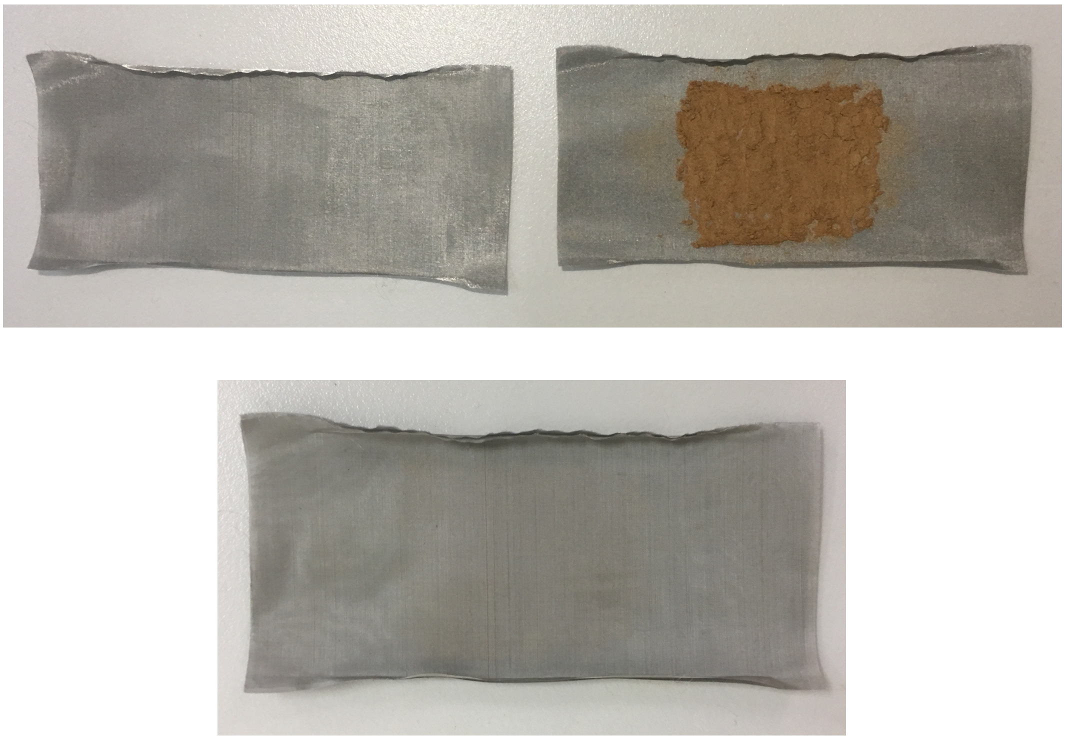

Figure 3.2 Preparation of the fuel samples on the meshes for combustion and pyrolysis experiments at wire mesh reactor (WMR). Top right figure shows stainless steel (SS316) wire mesh with hazelnut shell sample on it.

Table 3.1 Proximate, Ultimate, Elemental and Ash analysis of the studied samples.

Parameter	Hazelnut Shell (HS)	Olive residue (OR)	Soma lignite (SL)
Proximate analysis, wt.% as received			
Moisture	5.5	5.9	17.7
Volatiles	75.1	71.9	32.2
Fixed carbon[a]	18.5	17.4	37.0
Ash	0.9	4.8	13.0
Ultimate analysis, wt.% (daf)			
C	48.0	46.6	61.2
H	6.3	6.4	4.7
N	0.4	0.58	1.2
S	0.0	0.0	1.3
O[a]	45.4	46.4	31.7
Ash analysis, wt.% dry basis			
Si	1.48	4.6	31.6
Al	0.37	1.76	17.6
Fe	7.78	7.95	16.2
Ca	39.5	26.4	12.7
S	2.09	2.37	14.1
Mg	0.31	1.23	0.72
Mn	2.43	-	-
P	5.22	1.98	0.25
K	25.7	48.6	3.83
Na	-	-	0.46
Cl	-	4.46	0.06
Ash analysis, wt.% dry basis			
SiO_2	2.51	8.17	38.8
Al_2O_3	0.56	2.80	21.6
Fe_2O_3	7.36	7.31	8.89
CaO	38.6	24.8	7.87
SO_3	4.05	4.76	17.5
MgO	0.42	1.73	0.85
MnO	2.09	-	-
P_2O_5	9.39	3.69	0.29
K_2O	22.8	42.7	2.13
Na_2O	-	-	0.45
ZnO	12.2	0.58	-
Other oxides	0.03	3.46	1.60
Higher Heating Value, MJ kg^{-1} (fuel d.b.)	19.5	19.0	20.9
Low Heating Value, MJ kg^{-1} (fuel d.b.)	17.0	16.4	19.6

a: obtained by difference.

Table 3.2 summarizes the parameters which were chosen in the current work to investigate their effect on combustion and pyrolysis experiments of biomass and coal samples.

Table 3.2 Parameters which were chosen to study their effect on combustion and pyrolysis of fuel samples

	Moisture	Temperature	Heating rate
Hazelnut shell	✓	✓	✓
Olive residue	x	✓	✓
Soma lignite	x	✓	✓

3.2 Experimental Apparatus

In this study, wire mesh reactor (WMR) was the main apparatus where the combustion and pyrolysis experiments of biomass and coal samples were performed. Other than WMR, ashing furnace (see subsection 3.2.2) was used to obtain ash yields according to ASME standards which were compared with the results obtained from high heating WMR combustion experiments. Furthermore, thermogravimetric analyzer (TGA) (see subsection 3.2.3) was utilized to study reactivity of chars obtained from fast pyrolysis at WMR. Wire mesh reactor, ashing furnace and thermogravimetric analyzer were elaborated in the following subsections.

3.2.1 Wire Mesh Reactor (WMR)

Wire mesh reactor (WMR) shown schematically in Figure 3.2, was used under different conditions to carry out combustion and pyrolysis experiments at Clean Combustion Technologies Laboratory, Department of Mechanical Engineering at METU. During experiments, stainless steel (SS316) and high purity (>99.99%) molybdenum wire meshes were used as fuel holders. The wire meshes used in this study, had an aperture size of 40 μm (for SS 316 mesh with 25 μm wire diameter) and 60 μm (for molybdenum mesh with 35 μm wire diameter) which prevented loss of particles in the range of 106-125 µm. Two different mesh types were used due to their durability at different maximum temperatures, 1200 ^{0}C and 1600 ^{0}C. Wire mesh, was cut into sizes with an area of 75x40 mm in order to collect either ash or char yields.

In Figure 3.3 parts of the reactor are; 1- two wire meshes placed on top of each other to hold the sample in between and heat the sample, 2- R type thermocouple with 125 µm wire diameter was welded to the bottom mesh in order to measure the temperature, 3- electrodes which were made of copper to conduct current to the mesh, 4- a chamber that was made of glass to create a desired inert atmosphere for the pyrolysis, and 5- a vacuum pump in order to create vacuum inside the chamber which will then be filled with desired inert (N_2) atmosphere for the pyrolysis experiments. There is a lid on top of the chamber which has a quartz glass opening. Combustion experiments were performed using only chamber without the lid, while in pyrolysis experiments, lid was used in order to sustain vacuum condition.

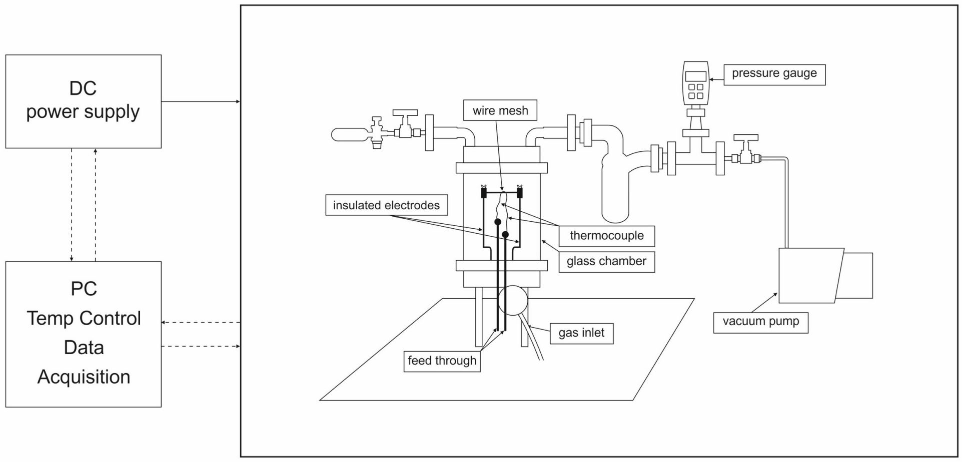

Figure 3.3 Schematic overview of wire mesh reactor (WMR).

Figure 3.4 Wire mesh reactor (WMR) in Clean Combustion Technologies Laboratory (CCTL).

Since atmosphere inside the glass chamber must be controlled in pyrolysis experiments, vacuum tight connection elements were used for the thermocouple and electrodes. Temperature values measured by thermocouple were recorded using LabVIEW software. R type thermocouple could operate up to 1768 °C and had a high accuracy, stability and a high response time with 10 000 µs (100 Hz). Thermocouple had 0.1 % of an error limit which corresponds to +/- 0.6 °C of temperature value that it reads. Composition of thermocouple wire alloys were 100% platinum for (+) and 13 % rhodium, 87 % platinum for (–).

In combustion and pyrolysis experiments, direct current (DC) welding machine, RCT 3500, (see Figure 3.5) was chosen as a power source to supply electrodes with high currents in order to heat the mesh. Therefore, during the experiments, where the machine was utilized under arc mode, positive and negative cables of the machine were connected to the electrodes. Welding machine has a maximum open circuit voltage (V_{OC}) of 85 V and amperage range of 20A-300A. RCT 3500 is an arc welding rectifier which is fabricated by Nuriş, a company producing welding machines in Turkey. RCT 3500 is mainly used in ship industry, construction areas and in other heavy industries.

Figure 3.5 Direct current (DC) power source. RCT 3500 arc welding rectifier.

Stainless steel (SS-316) wire mesh was utilized either in combustion experiments at 1040 °C and or in pyrolysis experiments at 1100 °C, while molybdenum mesh was used only in pyrolysis experiments at 1550 °C. In order to heat the stainless steel wire mesh up to 1040 °C (combustion experiments) and 1100 °C (pyrolysis experiments), power source was operated under 70 A and 80 A of current respectively, while for the molybdenum mesh, 155 A of current was chosen to achieve 1550 °C pyrolysis temperature.

In contrast to the work carried out by Anthony et al. [47], where the thermocouple was placed in between the meshes, in the present study to have an accurate temperature measurements, thermocouple was welded from the center of the bottom mesh as suggested by Hamilton et al. [48]. Welding was performed by using orthodontic spot welding machine shown in Figure 3.6, which was appropriate to weld thin wires of thickness 0.2-1.8 mm, with very low amperes (1mA – 2mA). In order to have a stable temperature measurements with low disturbances, firstly, thermocouple wires were welded by spot welding machine in a way that a point junction was obtained (see Figure 3.7). This step was performed carefully by using dental surgical binocular, to ensure of a point junction. Then the thermocouple was welded to the stainless steel (SS 316) or molybdenum mesh by using spot welding machine (see Figure 3.7).

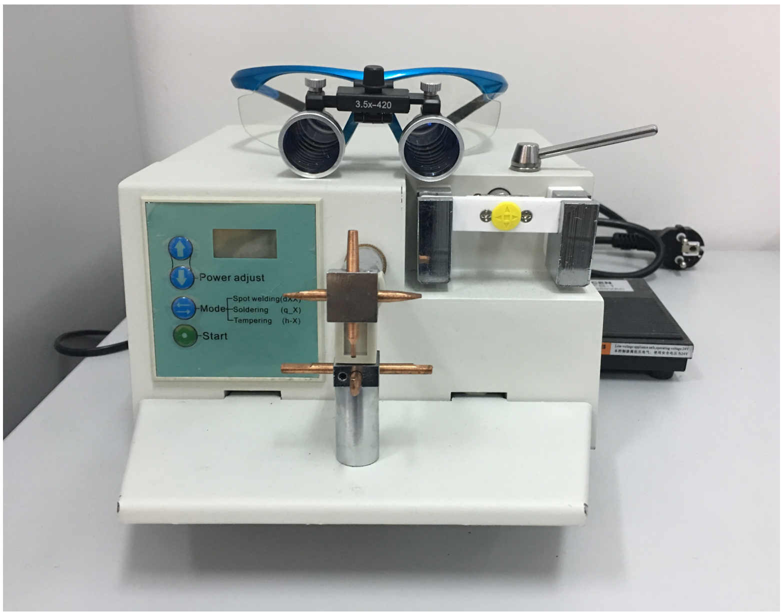

Figure 3.6 Orthodontic spot welding machine and dental surgical binocular.

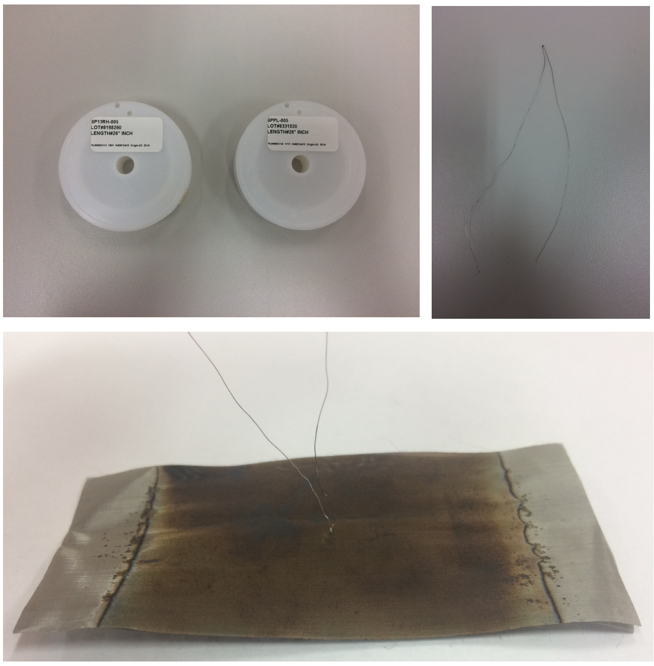

Figure 3.7 Welding thermocouple wires to each other and then to the stainless steel (SS 316) mesh by using orthodontic spot welding machine.

In order to determine heating rate values of pyrolysis experiments, trials without placing the fuel were conducted by utilization of stainless steel and molybdenum wire mesh at different power levels and obtained heating rates were summarized in Figure 3.8. Stainless steel wire mesh was performed at current levels of 65 A, 70 A, 75 A and 80 A, while molybdenum mesh at 150 A and 155 A.

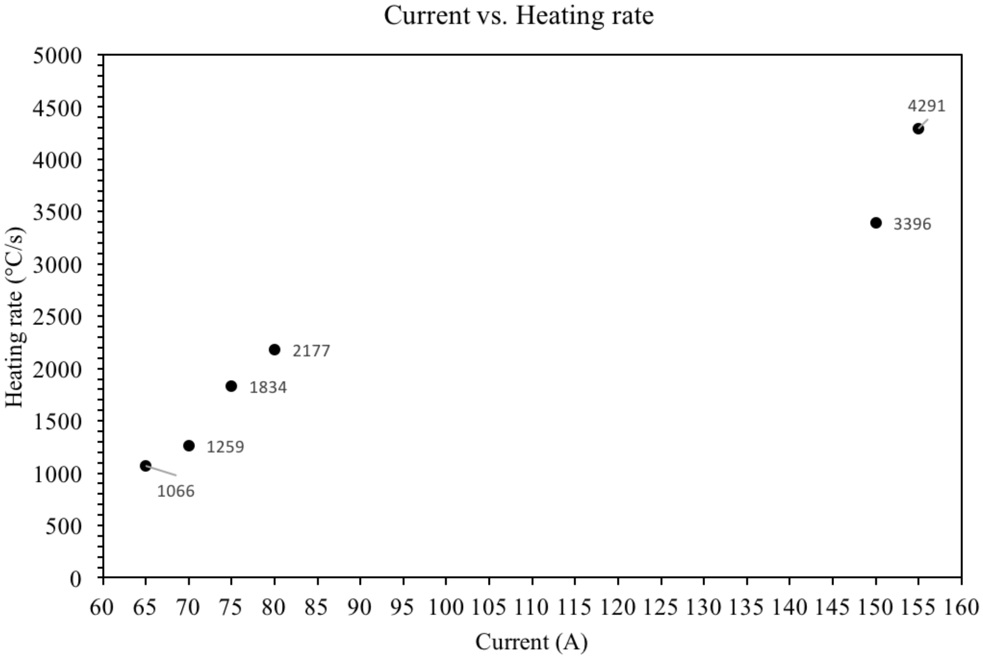

Figure 3.8 Heating rate values from pyrolysis experiments calculated by type R thermocouple. Stainless steel and molybdenum wire mesh were placed without the fuel.

Figure 3.9 shows stable temperature profiles of combustion at 1040 °C (1015 °C/s), pyrolysis at 1100 °C (2200 °C/s) with stainless steel (SS 316) wire mesh and pyrolysis at 1550 °C (4500 °C/s) with molybdenum mesh respectively. These trials were carried out at least three times without sample inside the mesh. Plots were obtained from LabView software. From the plots given in Fig. 3.9, it was proven that wire mesh reactor had a very rapid heating and cooling rates.

It is aimed to have a uniform temperature distribution over the mesh (reactor) when the heat is supplied. To study this phenomenon, R type thermocouple was welded to the different points of the stainless steel (SS 316) mesh (Fig. 3.10) and with several repetitions temperatures at these points were measured and results are tabulated in Table 3.3. These trials were carried out in an open air atmospheric condition and no fuel was placed to the mesh. It was observed that, points 1, 2, 3 indicated on the wire mesh (see Figure 3.11) which shows the vertical arrangement of the points, showed similar temperature readings which proves uniform temperature distribution along the vertical axis.

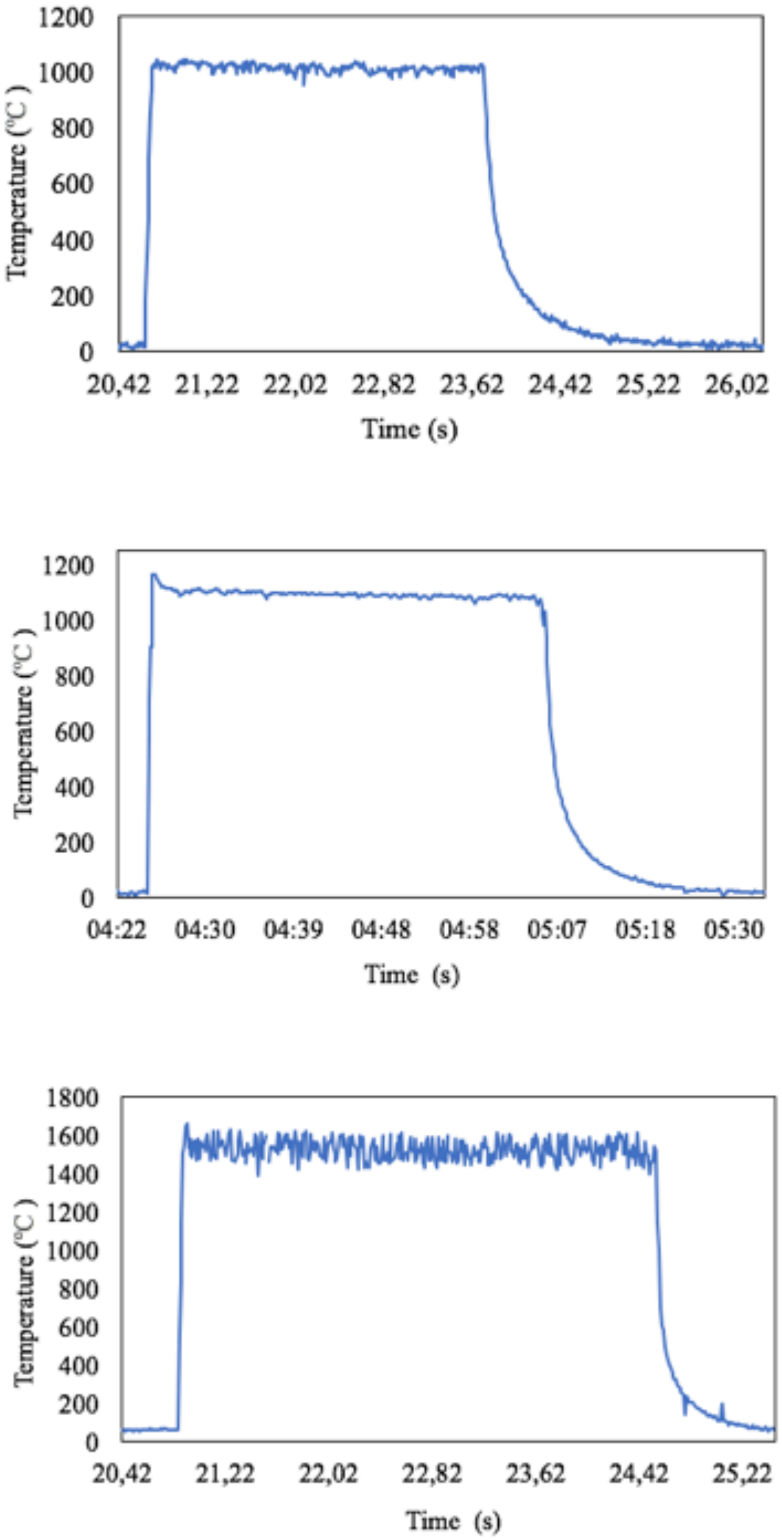

Figure 3.9 Temperature profiles of combustion and pyrolysis experiments without the sample. 1 st plot: Combustion at 1040 °C with SS 316 mesh. 2 nd plot: Pyrolysis at 1100 °C with SS 316 mesh. 3rd plot: Pyrolysis at 1550 °C with molybdenum mesh.

On the other hand, there was a slight decrease from middle section to the right and left corners of the mesh which was due to heat dissipation to the clamps (red circles). Therefore, the samples were placed in the vicinity of the points 1, 2 and 3 in order to have a uniform temperature distribution exposure to the fuels. Centrally placement of the fuels over the mesh was also suggested by Hoekstra et al. [54] and reported by Trubetskaya et al. [35].

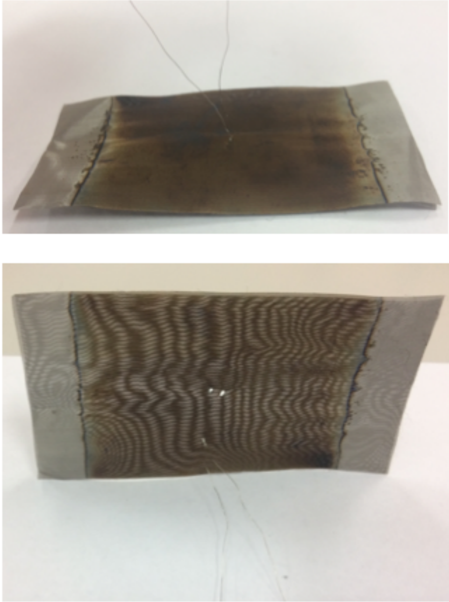

Figure 3.10 Welded thermocouple at the center (#1) and at the bottom (#3)

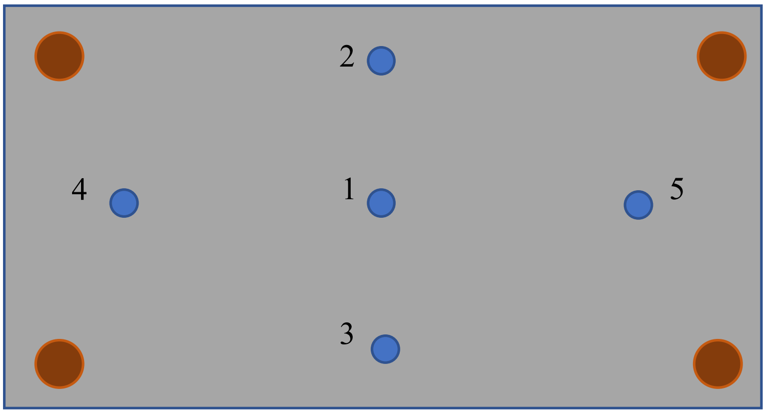

Figure 3.11 Temperature distribution over the reactor (top view). Red circles represent the clamps.

Table 3.3 Temperature measurements from different welded points obtained from R type thermocouple.

Points / **Trials**	**1**	**2**	**3**	**4**	**5**
1st Trial	1020 °C	1000 °C	1015 °C	750 °C	710 °C
2nd Trial	1020 °C	1100 °C	1012 °C	740 °C	710 °C

Temperature values that are shown above were temperatures of stainless steel wire mesh. Since the decrease of thermal gradient between the meshes was very rapid, it was assumed that mesh temperature, sample temperature and temperature of thermocouple junction were nearly identical throughout the experiments, as observed by Anthony et al. [47] and Hamilton et al. [48].

Moreover, trials together with the sample (hazelnut shell, HS) were also carried out to determine heating rate of the system. Lower heating rates but almost same temperature (1050 °C) values were recorded. Figure 3.12 shows the heating rate data obtained from combustion tests with and without sample cases. It is clear that, when the sample (Hazelnut shell, HS) was placed, heating rate decreased dramatically. However, temperature stayed almost at the same level as illustrated in Fig. 3.13, which is temperature profile of hazelnut shell combustion at 70 A (1050 °C). The reason of having lower heating rate could be due to energy that was required to heat the biomass and energy for endothermic pyrolysis reactions [54], [55].

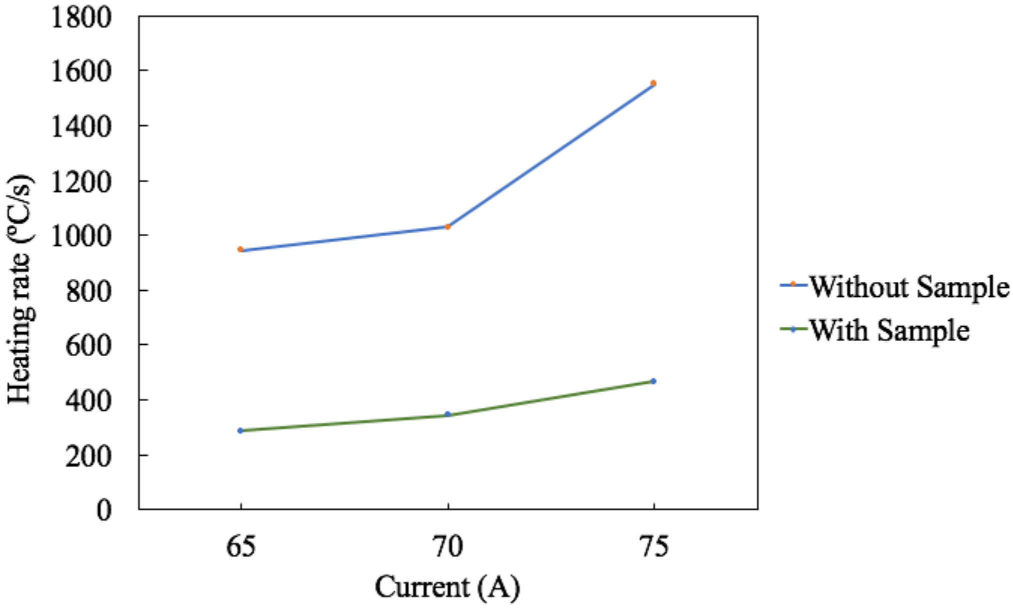

Figure 3.12 Heating rate data obtained from combustion trials with and without sample (hazelnut shell, HS) cases.

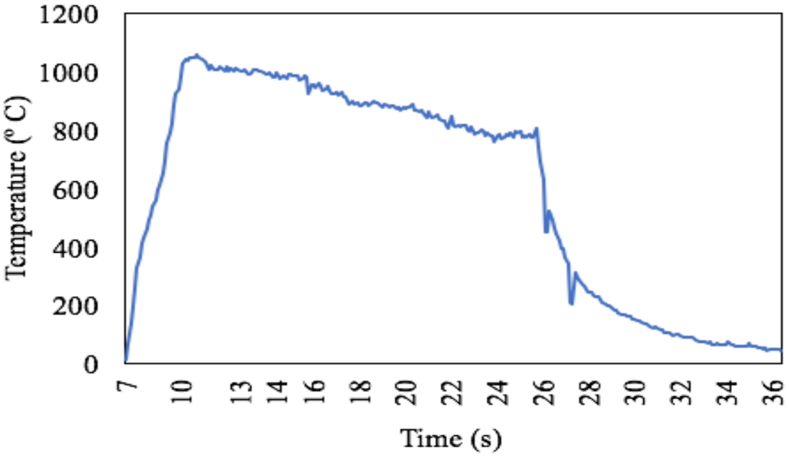

Figure 3.13 Temperature profile of hazelnut shell (HS) combustion at 1050 °C (70 A).

3.2.2 Ashing Furnace

Ashing furnace, is a widely used laboratory furnace in order to determine ash yield of a material. Biomass, coal, rubber, plastics can be ashed and tested in the ashing furnace. Crucible with sample inside is placed in a muffle furnace and then is heated up to the relevant temperature under low heating rates. Depending on its brand, maximum temperatures of 1100 °C or much higher temperatures around 1600 °C can be obtained. According to the type of the sample, there exist ashing procedure standards developed by ASTM International (American Society for Testing and Materials), standards developing organization.

In the present study, prortherm furnace, shown in Figure 3.14, fabricated by Protherm Furnaces company was used to perform ashing experiments of biomass and coal samples in Clean Combustion Technologies Laboratory (CCTL) of Mechanical Engineering Department at METU. Furnace has a 1600 °C of max working temperature and high level of temperature uniformity.

Figure 3.14 Protherm ashing furnace at Clean Combustion Technologies Laboratory (CCTL)

Ashing of biomass (Hazelnut shell, HS and Olive residue, OR) and lignite (Soma lignite, SL) samples were carried out according to ASTM E1755-01 and ASTM D3174-12 standards respectively. During the ashing procedures, amount of biomass and lignite samples was kept low at 1 g.

Based on ASTM E1755-01 standard for biomass, samples were heated from ambient temperature to 250 °C at 10 °C/min and then were held at that temperature for 30 min. In the next stage, samples were heated to 575 °C at around 8 °C/min and were held at 575 °C for 2 hours. At the end of 2 hours, crucible was removed and was cooled to room temperature in desiccator. Procedure was illustrated in the plot given by Fig. 3.15.

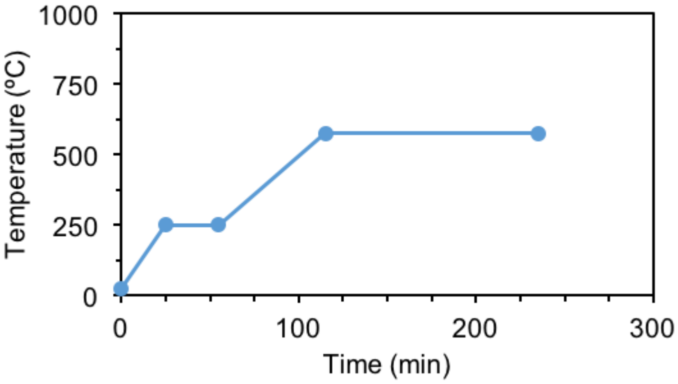

Figure 3.15 ASTM E1755-01 standard ashing procedure for biomass samples

In contrast to biomass, coal samples were heated to 500 °C at nearly 8 °C/min in 1 hour according to ASTM D3174-12 standards. Procedure was continued by heating the samples from 500 °C to 750 °C at the same heating rate in 1 hour. Then the samples were held at 750 °C for 2 hours. Afterward, crucible was removed and left inside the desiccator to cool down at room temperature. Figure 3.16 shows the ashing procedure of lignite based on ASTM D3174-12 standards.

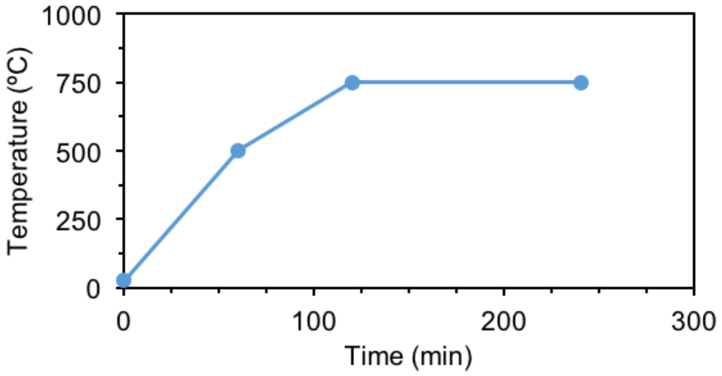

Figure 3.16 ASTM D3174-12 standard ashing procedure for lignite samples

3.2.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA), is a widely used rapid and easy technique which studies combustion characteristics and kinetic parameters of solid fuels when they are burned or pyrolyzed under low heating rate conditions. From thermogravimetric analysis, volatile matter, moisture content, decomposition temperature, ash content, carbon content of a sample can be obtained. TGA provides weight loss of a sample as a function of time and temperature at low heating rates. Therefore, results from TGA are not close to the ones obtained from industrial power plants.

Inside the TGA equipment (see Fig. 3.17), there is a ceramic furnace with a sample pan which is placed above the precision balance and supported by a support rod called stem [56]. Maximum temperature that can be reached in TGA is around 1200 °C which depends on the brand of the equipment. Thermocouple that is attached to the pan from the bottom, measures temperature of a pan. Since the experiments are performed under low heating rates, it is assumed that the sample has an identical temperature with the pan. During the experiments, sample environment is controlled with a purge gas which can be an inert or a reactive gas.

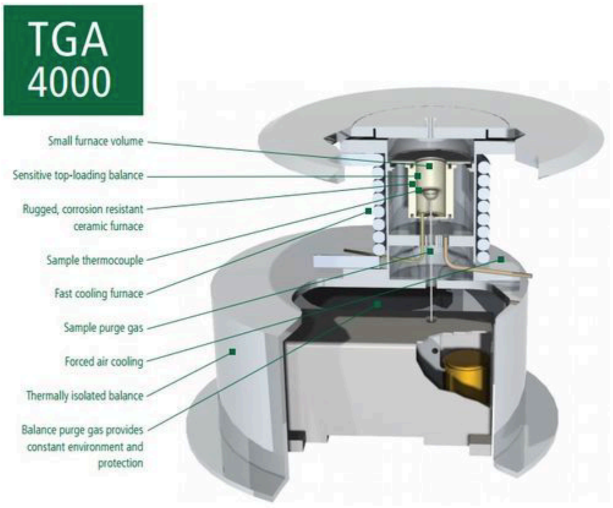

Figure 3.17 Schematic representation of Thermogravimetric analyzer (TGA)

3.3 Experimental Approach

Chosen biomass and coal fuels were either 1) burned in combustion experiments or 2) pyrolysed in pyrolysis experiments in this set up. Main focus in the combustion experiments was to study ash yield, its morphology and chemical composition, while in pyrolysis experiments volatile yield, char morphology, char chemical kinetic analysis were investigated. Prior to any combustion and pyrolysis experiments, meshes were pre-heated without the sample up to the temperature of which samples were burned or pyrolysed. At the end of experiments, if the mesh was convenient for another trial, same mesh was used in the new experiment for the same fuel providing that the mesh was cleaned quite well by using air compressor. If the mesh was damaged, the new one was used. Table 3.4 and Table 3.5 summarize combustion and pyrolysis conditions that were performed in this study. Combustion and pyrolysis methodologies will be outlined separately in the subsections.

Table 3.4 Temperature values of combustion experiments of the fuels.

Experimental Rig Fuel	Ashing Furnace (Standard)	Combustion in WMR
Hazelnut Shell (HS)	575 °C	1040 °C
Olive Residue (OR)		
Soma Lignite (SL)	750 °C	

Table 3.5 Temperature values of pyrolysis experiments of the fuels.

Experimental Rig Fuel	Pyrolysis in WMR
Hazelnut Shell (HS)	1100 °C and 1550 °C
Soma Lignite (SL)	1100 °C
Blend (SL+HS)	1100 °C

3.3.1 Combustion Experiments

Combustion experiments were conducted to obtain ash yields. Low and high heating rate combustion experiments were conducted by using ashing furnace (10 °C/min) and WMR (1015 °C/s) respectively (see Figure 3.18 for WMR).

Ash yield is the remaining solid residue transformed from organic and inorganic constituents of coal or biomass when they are subjected to thermal processes [57]. In the present study, combustion experiments of different coal and biomass fuels were performed in WMR with settled residence times.

Obtained ash yields were calculated according to following equation (3.1).

$$\text{Ash Yield [wt.\%]} = \frac{m_{\text{mesh+ash}} - m_{\text{final mesh}}}{m_{\text{mesh+biomass/coal}} - m_{\text{initial mesh}}} * 100 \tag{3.1}$$

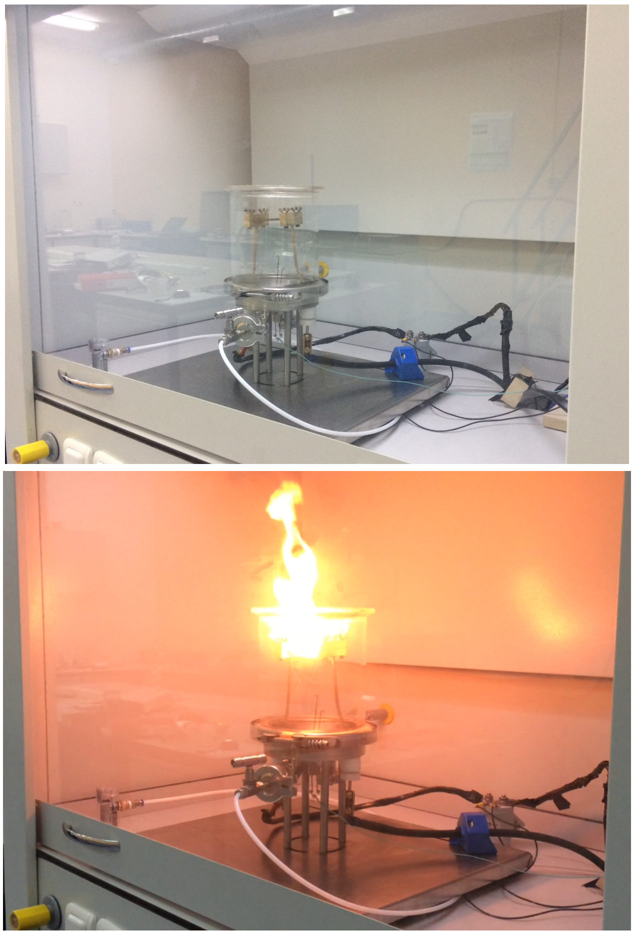

Figure 3.18 Combustion of hazelnut shell (HS) at 1040 ºC (1015 ºC/s) by using stainless steel wire mesh.

Samples were placed in between two stainless steel (SS-316) wire meshes especially to the middle part of the mesh in a single layer after measuring their weights by using analytical balance TLE 104 with a readability of 0.1 mg shown in Fig. 3.19. Samples were burned at 1040 ºC temperature with the heating rate of 1015 °C/s. During the experiments, to prevent disturbance from surrounding flows chamber was used which was open to the atmosphere. At least three repetitions of each combustion experiments were performed. In order to decide for the residence time of complete combustion of the fuels, several experiments were carried out with the same amount of sample but with different holding times. Residence times for the complete combustion of different fuels were chosen when the ash yield left on the mesh at the end of experiment stayed at the constant value. Residence times of 13 s, 12 s, and 26 s were decided for complete combustion of hazelnut shell (HS), olive residue (OR) and soma lignite (SL) respectively. Following plots depict data related to ash yields obtained from biomass and lignite combustion experiments in WMR at 1040 ºC at different holding times (Fig. 3.20).

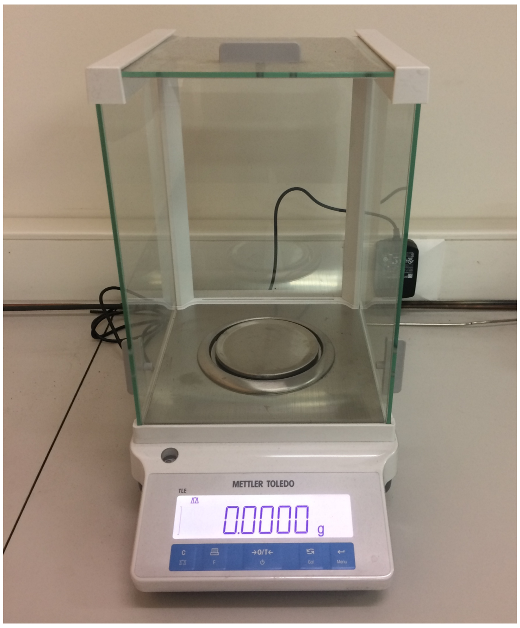

Figure 3.19 Analytical balance ME 54 with a readability of 0.1 mg.

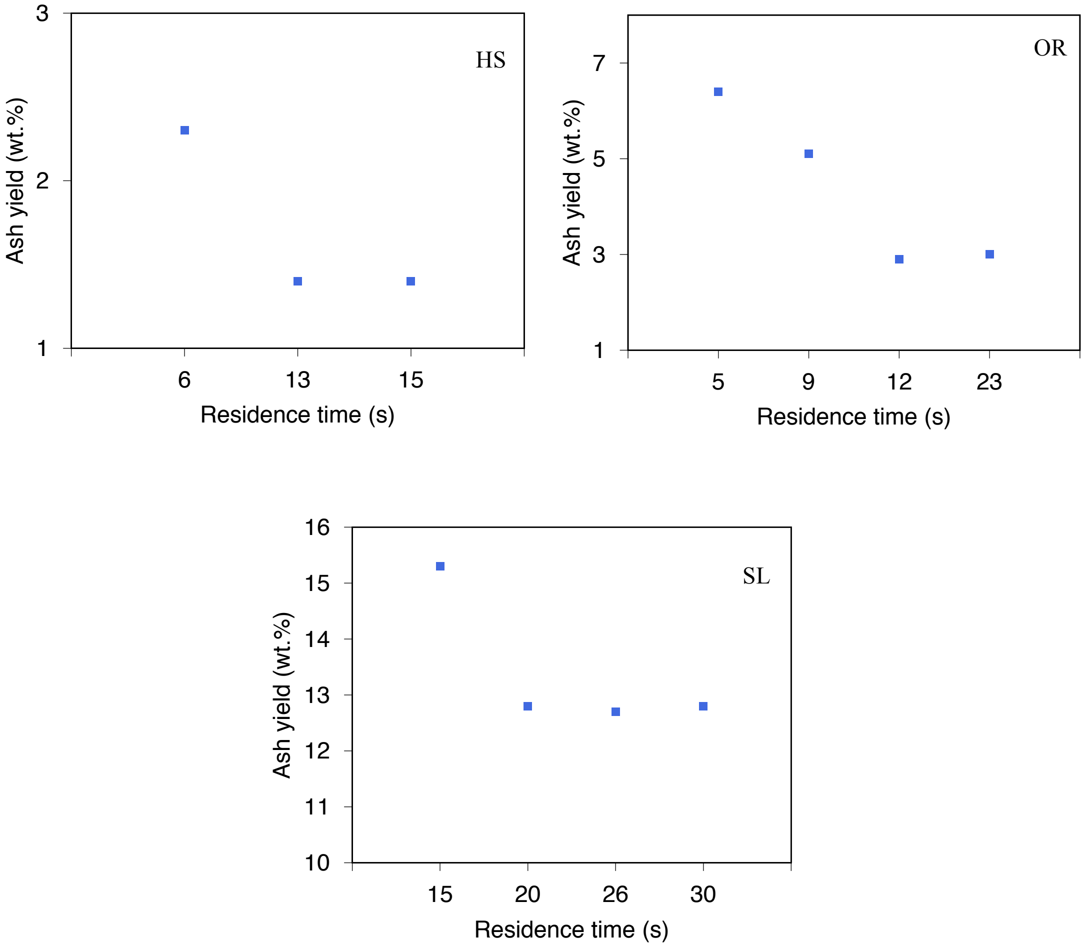

Figure 3.20 Influence of residence time on ash yields obtained from combustion experiments of hazelnut shell (HS), olive residue (OR) and soma lignite (SL) in WMR at 1040 ºC.

Since the ash yields left at the end of experiments were not enough for the analyses techniques such as SEM/EDS, TGA, BET, ash from repetitive experiments were united and contained in small sealed vials.

3.3.2 Pyrolysis Experiments

Several pyrolysis experiments were carried out under two different temperature (SS 316 mesh: 1100 ºC, Molybdenum mesh: 1550 ºC) conditions for different fuels with the particle size range of 106-125 µm by using wire mesh reactor (WMR) (see Fig.

3.21). In the experiments, heating rates were around 2200 ºC/s and 4500 ºC/s for stainless steel mesh and molybdenum mesh respectively.

Figure 3.21 Pyrolysis at 4500 ºC/s by using molybdenum wire mesh. In the first image, no sample was placed. In the second image, hazelnut shell (HS) was pyrolyzed at 1550 ºC.

In pyrolysis experiments, first step was to create a vacuum inside a glass chamber by using a vacuum pump. Then the chamber was filled with desired inert Nitrogen atmosphere from the tanker (see Fig. 3.22) up until pressure inside the chamber reaches to surrounding pressure of approximately 1 atm.

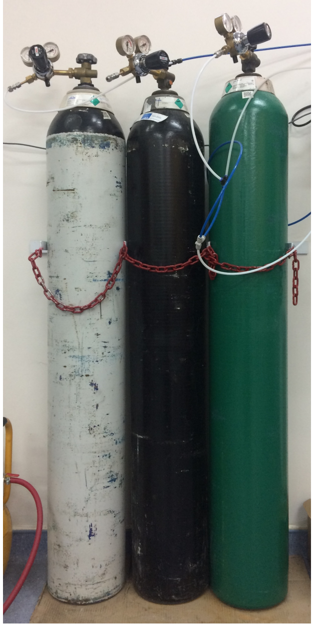

Figure 3.22 Gas cylinders located at Clean Combustion Laboratory. Green one is nitrogen cylinder used in pyrolysis experiments.

Char yield which comprises of ash, unburned carbon and some little amount of oxygen and hydrogen, is non-devolatilized solid residue left from pyrolysis of coal or biomass. Chars obtained from fast pyrolysis of hazelnut shell, soma lignite and their blends under two different heating rate conditions (2200 °C/s and 4500 °C/s) were calculated by using equation (3.2) and analyzed in terms of their volatile yield, chemical kinetics, morphology and BET surface area. For the validation purpose, obtained char contents were compared with the summation of ash and fixed carbon content of corresponding fuels from proximate analysis. In order to understand effect of moisture content over the hazelnut shell chars, both dried and as received fuels were used in the experiments. Moisture content of as received hazelnut shell was 5.5%, and was determined from proximate analysis. To get the dried fuel, as received parent fuel (HS-A) was left overnight in the oven at 150 ºC temperature. Obtained fuel is named as dried hazelnut shell and titled as HS-D in this study.

$$\text{Char Yield [wt.\%]} = \frac{m_{\text{mesh+char}} - m_{\text{final mesh}}}{m_{\text{mesh+biomass/coal}} - m_{\text{initial mesh}}} * 100 \qquad (3.2)$$

To calculate the volatile yield at the end of pyrolysis experiments, char and moisture contents of a fuel were subtracted from the sample amount used in the experiment, as expressed in the following equation (3.3).

$$\text{Volatile Yield [wt.\%]} = [1 - \text{char}_{\text{wt.\%}} - \text{moisture}_{\text{wt.\%}}] * 100 \qquad (3.3)$$

Pyrolysis experiments of hazelnut shell (HS) and Soma lignite (SL) samples were conducted with low residence time, 5 seconds, at high temperature (1100 ºC, 1550 ºC) and high heating rate (2200 ºC/s, 4500 ºC /s) conditions. To decide on minimum residence time for complete pyrolysis of HS and SL samples, preliminary analyses were performed at different holding times. Volatile yield content almost stayed at a constant value for residence times above 5 seconds for both HS and SL as depicted in Figure 3.23 and Figure. 3.24. Therefore, pyrolysis experiments of hazelnut shell, soma lignite and their blends were conducted for 5 seconds.

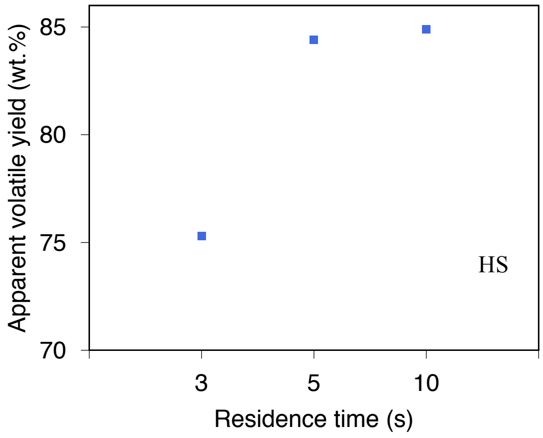

Figure 3.23 Influence of residence time on volatile yield of hazelnut shell (HS) pyrolyzed in WMR at 1100 ºC.

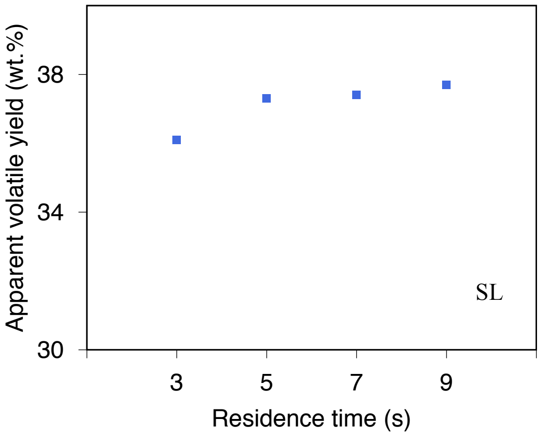

Figure 3.24 Influence of residence time on volatile yield of soma lignite (SL) pyrolyzed in WMR at 1100 ºC.

In this study, errors of experimental trials in either combustion or pyrolysis experiments were calculated and found out to be low (≤ 1 wt. %). Therefore, error bars were not shown in the figures 3.20, 3.23 and 3.24. However, for the sake of representation, error bars were shown in the figures 4.2 and 4.3, where they show standard deviation from the mean of experimental trials in pyrolysis in WMR and represent 98% confidence statistical error. Errors may have originated from possible inaccuracies in determining ash yield or char yield during weighing step or it could be due to experimental preparation step or any particle loss during combustion/pyrolysis experiments. It was concluded that WMR experiments were repetitive.

3.4 Analysis Techniques

At the end of combustion and pyrolysis experiments ash yields and char yields were obtained respectively. Analysis techniques which are used to study the yields are outlined in the following subsections.

3.4.1 Analysis Techniques for Ash Obtained from Combustion Experiments

In order to investigate changes in morphology and in chemical composition of the ashes obtained under two different heating rates, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed respectively at Central Laboratory at Middle East Technical University. Same analysis techniques were conducted for parent fuels in order to study the changes in morphology and composition of yields. Since biomass parent fuels (HS: hazelnut shell, OR: olive residue) had low amount of ash content, obtained ash yields from WMR were low. Since this amount of ash was not enough for x-ray fluorescence (XRF) analysis, which gives a more detailed chemical composition information, EDS was performed to get an insight into the chemical compositional changes.

3.4.1.1 SEM/EDS

Scanning electron microscope (SEM), is a microscope which uses focused electron beam to generate high resolution images of solid conductive samples in a vacuum condition. It was designed because of limitations of Light Microscopes. SEM enables researchers to examine micro-scale, nano-scale characteristics of sloid specimens. Information like, topography, morphology, and crystallography of a sample can be obtained from SEM analysis. In SEM, electron beam with high energy produced by electron gun is hit to the surface of a sample in order to obtain maximum signal for detection. When the electron beam is interacted with the specimen, X-rays, backscattered electrons, secondary electrons, Auger electrons are emitted. Backscattered electrons and Secondary electrons are the strongest signals in SEM. Backscattered electrons are generated due to elastic collision of electrons at a depth of 30-40 nm. Secondary electrons escape from the depth of 10-20 nm of a sample and carry information about surface topography of a sample which is used in SEM imaging. Energy-dispersive X-ray spectroscopy (EDS) analysis, is performed to obtain elemental, chemical composition of a solid material. Its working principal is based on the detection of emitted X-rays from the sample.

In this study, SEM and EDS analysis were performed at Central Laboratory at METU. FEI Quanta 400 F Scanning Electron Microscope was used to generate SEM images and to get elemental composition of the ashes obtained from WMR and ashing furnace.

Since the materials must be conductive for SEM and EDS analyses, after placing nonconductive samples on carbon tapes, coating by Au/Pd were conducted. Coating the samples inhibits charging effect and generates images with a good contrast.

3.4.2 Analysis Techniques for Char Obtained from Pyrolysis Experiments

Biomass and lignite chars obtained from high heating rate (2200 °C/s, 4500 °C/s) pyrolysis experiments conducted at WMR, were analyzed in terms of morphology, elemental composition, surface area and reactivity.

3.4.2.1 SEM/EDS

Morphology and elemental composition of obtained chars were investigated by performing SEM and EDS analyses. Results were obtained by using FEI Quanta 400 F Scanning Electron Microscope at Central Laboratory at METU. EDS analyses were conducted by choosing 10 different spots on a sample and averaging chemical composition information of these spots.

3.4.2.2 BET

In order to study influence of pyrolysis conditions (high temperature and high heating rate) on chars, Brunauer–Emmitt–Teller (BET) surface area and pore size characterization analyses of obtained chars were carried out at Central Laboratory at METU. In BET analysis, specific surface area of a sample is going to be determined.

Prior to BET analysis, char samples left to degas at 150 °C for 3 hours. Then the chars subjected to nitrogen gas in order to obtain adsorption isotherms. Isotherms showed amount of adsorbed nitrogen at a specific pressure. By using these isotherms, volume of the adsorbed nitrogen gas by the surface of the chars was determined. These gave the total surface area of the chars including the pores in the sample. From nitrogen gas adsorption, volume distribution of pores was also determined.

3.4.2.3 TGA

In the current study, Perkin Elmer brand TGA apparatus with the model of Pyris STA 4000 (see Figure 3.25) at the Department of Aerospace Engineering at METU, was used to conduct isothermal char combustion experiments and to study burnout profiles of the chars. High heating rate (2200 °C/s, 4500 °C/s) pyrolysis experiments of biomass (hazelnut shell, HS), coal (Soma lignite, SL) and blended samples were conducted at wire mesh reactor (WMR) and chars were collected. In order to study effect of moisture on the burnout profiles of hazelnut shell chars, both dried and as received hazelnut shell char samples (HS-D and HS-A) were used in TGA analysis.

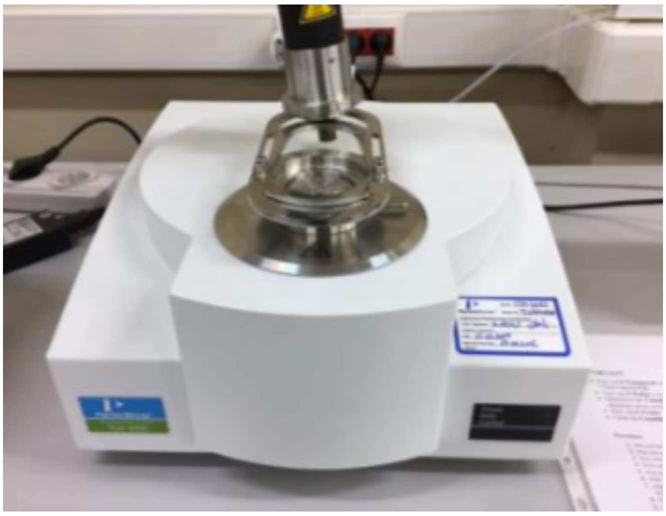

Figure 3.25 TGA Pyris STA 4000 from Perkin Elmer at the Department of Aerospace Engineering.

Prior to isothermal char combustion at TGA, char samples were heated from 30 °C of ambient temperature to combustion temperatures (400 °C for biomass chars (HS), and 450 °C for coal (SL) and blended chars) under 30 °C/min of heating rate and 20 ml/min nitrogen flow conditions. This stage ensured that any volatile or moisture left in the chars was removed. As suggested by Kazanç et al. [22], in order to reduce influence of diffusion during combustion stage, very low amount (2-2.5 mg) of char samples was put inside the sample pan. Moreover, according to Hindmarsh et al. [58], coal combustion takes place under chemically controlled regime in the temperature range of 673-823 K. Therefore, prior to TGA analysis, preliminary tests were conducted to decide on appropriate char combustion temperature in order to have chemically controlled char oxidation.

After the heating stage, samples were held for 3 min at the combustion temperature for the system to be stabilized. Afterwards, isothermal combustion of the chars was performed and gas flow was switched from nitrogen to air with the flow rate of 100 ml/min. Isothermal combustion stage for hazelnut shell chars was set to last for 120 min, however, chars were completely burned in almost 30 minutes. It was decided when the weight (%) vs. time curve maintained the constant level. Soma lignite and blended chars burned isothermally for 600 min at 450 °C.

Obtained TG curves were used to calculate carbon burnout by using following equation (3.1),

$$\text{burnout} = \frac{w_0 - w_t}{w_0 - w_f} \tag{3.1}$$

where w_0 stands for the initial weight, while w_t and w_f stands for the weight at the time t and at the end of isothermal combustion respectively.

In the current work, thermal decomposition and combustion of coal and biomass samples were considered to be modelled by widely applied first order reaction rate equation (3.2).

Reaction rate equation: $r = \frac{\partial \alpha}{\partial t} = k * f(\alpha) = k(1 - \alpha)$, (3.2)

$$\alpha = 1 - \frac{C}{C_0} \tag{3.3}$$

where,
k: reaction rate constant
f(α): function of reaction mechanism
α: degree of conversion of a sample
dα/dt: rate of conversion
C_0: initial carbon weight
C: Carbon weight at time t

As reported by Pottmair et al. [59], the rate of conversion is proportional to the unreacted material (1 – α), with the reaction rate constant k the proportionality constant. In order to calculate the rate constants for isothermal combustion, in the first step, equation (3.3) was integrated with initial conditions of α = 0 and t = 0 and equation (3.4) was obtained. Then, from the slope of the –ln (1 – α) vs t plots, rate constants were calculated. As considered by Pottmair et al. [59], "reference values for reaction conversions were taken between 0.05 and 0.95 ($k_{5-95\%}$) and the conversion time for the reaction at 0.9 ($t_{90\%}$)."

$$-\ln(1 - \alpha) = k * t \tag{3.4}$$

CHAPTER 4

RESULTS AND DISCUSSION

Results obtained from combustion and pyrolysis experiments of Turkish fuels conducted at wire mesh reactor (WMR) are discussed in this section (see subsection 4.1 and 4.2, respectively).

During combustion, the wire mesh set-up was open to air and surrounded by a chamber to prevent disturbances of the flow. Combustion experiments were carried out at 1040 °C and heating rate of 1015 °C/s. Hazelnut shell (HS), olive residue (OR) and Soma lignite (SL) were burned and analyzed in terms of ash yield, ash morphology, and ash chemical composition. The effect of fuel type, temperature, and moisture content on the aforementioned parameters is discussed in subsection 4.1.

In WMR pyrolysis, the chamber was filled with nitrogen to provide an inert atmosphere, and experiments were conducted at high temperature (1100 ºC and 1500 ºC) and high heating rate (2200 °C/s and 4550 °C/s). Hazelnut shell (HS), Soma lignite (SL), and their two different blends with mixtures of 50 wt.% HS – 50 wt.% SL and 25 wt.% HS – 75 wt.% SL, were used. Volatile yields, char morphology, char chemical composition, char reactivity, and char oxidation kinetics were obtained. The effect of parameters such as fuel type, coal-biomass blending ratio, atmosphere temperature, and heating rate are discussed in subsection 4.2.

4.1 Combustion of Fuels

In this subsection, the effect of fuel type, temperature, and moisture content on the ash yield, ash morphology, and ash chemical composition is evaluated and discussed.

Combustion of hazelnut shell (HS), olive residue (OR) and Soma lignite (SL) was carried out in the wire mesh reactor under high temperature (1040 °C) and high heating rate (1015 °C/s) conditions. Ashes were compared with ashing furnace and standard proximate analysis results for validation.

4.1.1 Ash Yield

Table 4.1 depicts the ash yields obtained from the combustion experiments in WMR, ashing furnace, and proximate analysis (PA). The test conditions are also included to ease the comparison between each method. Ash yields from high heating rate (1015 °C/s) experiments conducted in the WMR were compared with the ones from low heating rate (~10 °C/min) ashing furnace (plateau temperature of 575 ºC for biomass, and 750 ºC for coal samples) and proximate analysis (plateau temperature of 950 ºC).

The ash yield obtained from combustion of hazelnut shell (HS) was 1.4 wt.% at high heating rates (1015 °C/s) in WMR and was similar to those from low heating rate (20 °C/min) ashing furnace (1.8 wt.%) and proximate analysis (0.9 wt.%). Similarly, the yields from SL were similar and independent of the heating rate. Ash yield of SL obtained from WMR was 12.7 wt.%, and matched the yields from ashing furnace and proximate analysis (13.1 and 13.0 wt.%, respectively).

Although the yields were similar between methods for HS and SL, olive residue (OR) displayed a different trend. Ash yield of OR from WMR (2.9 wt.%) was nearly 1.5 times lower than those from either ashing furnace and proximate analysis (4.5 wt.% and 4.8 wt.%, respectively). The pronounced decrease of OR ash yield with increase in heating rate was related to the significant loss of K content (see Table 4.2). A rapid evaporation of potassium oxide (K_2O) above 900 °C, may cause low K content in the ash yield of olive residue (OR) obtained from 1040 °C WMR combustion, as explained by Misra et al. [60], and elaborated in subsection 4.1.3. of this study.

Table 4.1 Ash yields from WMR, ashing furnace and proximate analysis

	Wire Mesh Reactor		**Ashing Furnace**	**Prox. Analysis**
Fuels	**1040 °C,** **1015 °C/s**		**575 °C for biomass (~150 min),** **750 °C for lignite (~125 min),** **~10 °C/min**	**950 °C,** **20 °C/min,** **(~8 min)**
	Residence time (s)	**Ash yield (wt.%)**	**Ash yield (wt.%)**	**Ash yield (wt.%)**
HS	12	1.40	1.80	0.900
OR	13	2.90	4.50	4.80
SL	26	12.7	13.1	13.0

4.1.2 Ash Morphology

SEM micrographs of the ashes are illustrated in Figure 4.1. The influence of low and high heating rates on physical structures of the obtained ashes is discussed in this subsection. Biomass ashes obtained from WMR (1015 °C/s) and ashing furnace (10 °C/min) displayed similar morphology. SEM micrographs of OR ash obtained from low and high heating rate combustion experiments had a more skeletal structure which may be due to different mineral composition. However, HS ash morphology from both low and high heating rate combustion experiments does not present these structures and shows clear signs of high fluidity. According to Trubetskaya et al. [35], due to bridge- breaking and formation of cross links in biomass at high heating rates, molten biomass structure may be formed. For the case of SL ash from ashing furnace (Figure 4.1. 3e, 4e), since it was rich in Al (3.95 wt.%) and Si (6.16 wt.%), as well as Ca (0.90 wt.%) and Fe (0.82 wt.%), the main elements that affect the melting behavior of ash, more molten structures with lapped layers were observed, in line with results by Wu et al. [61]. Some small fragment on the main particles were noticed, which might be related to the soot formation. In contrast to SL ash from ashing furnace, the one from WMR (Figure 4.1 2f, 3f, 4f) showed agglomerated structure which prevented ash fluidity. Such appearance can be attributed to aggregation of mineral composition (Si, Al, Ca, Na, Fe, S, etc.) [62] at high temperature (1040 °C) combustion experiment [63].

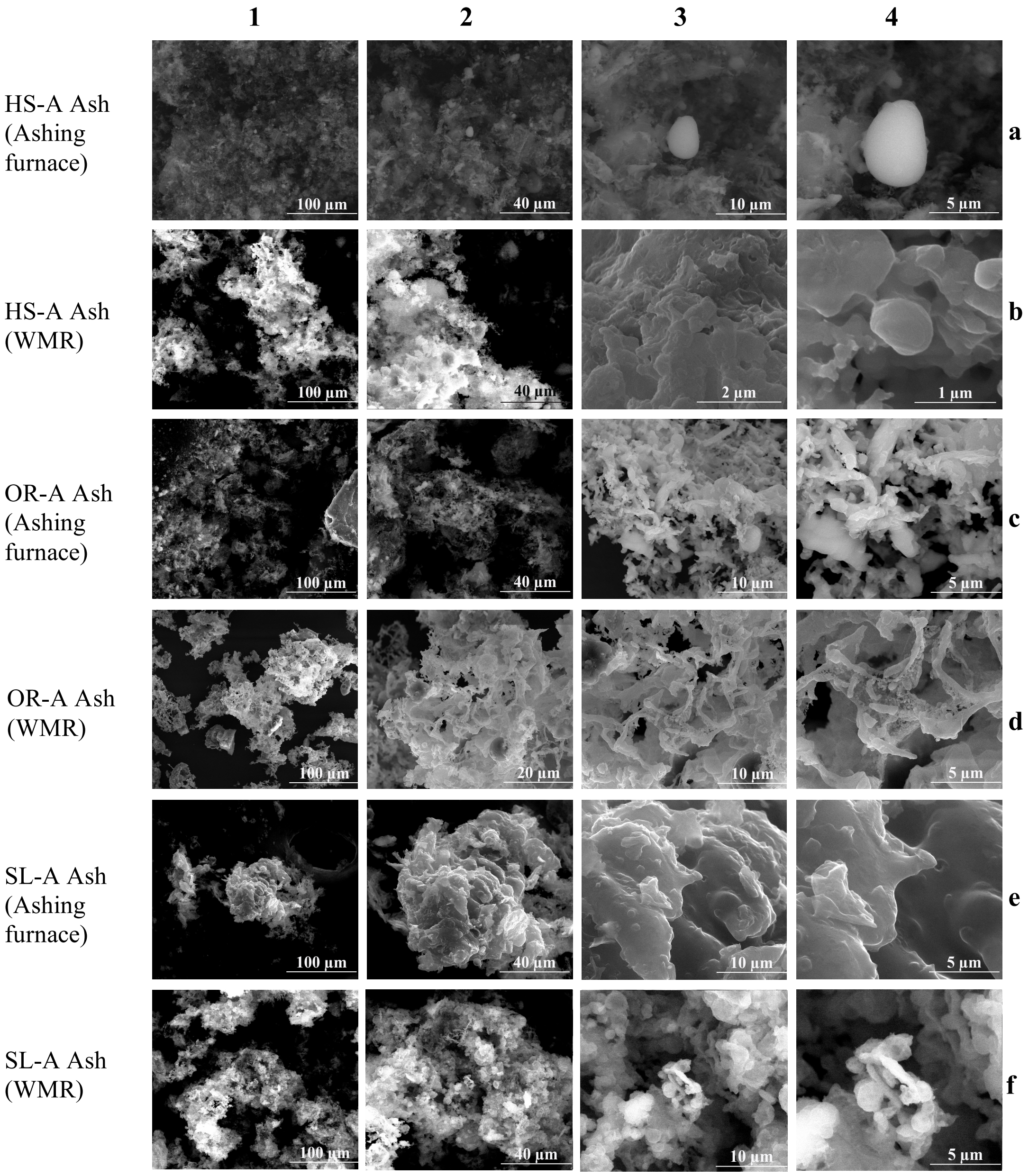

Figure 4.1 SEM images of ash yields of biomass (HS, OR) and lignite (SL) samples obtained from low heating rate (10 °C/min) ashing furnace and high heating rate (1015 °C/s) WMR (-A as received, -D dried fuel).

4.1.3 Ash Chemical Composition

Table 4.2 shows EDS (energy dispersive x-ray spectroscopy) results of the ashes obtained from experiments conducted at low and high different heating rates. Results are in carbon and oxygen free basis. Elemental compositions were normalized according to ash percentage obtained either from WMR or ashing furnace. EDS results showed that lignite was rich in aluminum and silica with almost 4 wt.% and 6 wt.% of the parent fuel, respectively. However, in the ashes from biomass fuels, the amount of Al and Si was low (0.1 wt.% and 0.2 wt.% respectively), whilst K and Ca were high (~0.5 wt.% of K and Ca for HS; ~1.5 wt.% of K and 0.6 wt. % of Ca for OR), and were thus the main ash forming elements in biomass. Other elements in HS ash such as Mg, Fe, P, Si were present in negligible amount (cf. Table 4.2).

The temperature had a significant effect on the chemical composition of HS, OR, and SL. For HS, the higher content of Cr from WMR as compared to ashing furnace can be attributed to the effect of high temperature (>1000ºC) that results in high chromium content in the fly ash as observed by Swietlik et al. [64]. Moreover, the presence of high alkali elements in biomass may have resulted in deposition of oxidized Cr (III) over the surfaces of fly ash particles [64]. Combustion temperature had a significant effect on the concentration of potassium of both HS and OR. An increase in the temperature from 575 ºC (ashing furnace) to ~1000 ºC (WMR) decreased the potassium concentration in both HS and OR ash from 0.71 wt.% and 2.36 wt.%, respectively, to 0.3wt.% and 0.99 wt.%, respectively. As reported by Misra et al. [60], above 900 °C, potassium oxide (K_2O) evaporates immediately when the dissociation of potassium carbonate (K_2CO_3) takes place, which may be the reason of the low content of K in HS and OR ash from WMR.

In OR ash from WMR, besides the decrease in K, a significant reduction in the concentration of Cl and S was also observed. Cl available in biomass are volatile and, at high temperature, KCl sublimation may occur which consequently decreases both Cl and K content in the final remaining ash [65]. A significant decrease of S content in OR ash obtained from WMR, is associated with the devolatilization of alkali metal sulfates [24]. For HS however, the sulfur content was too low for detection and comparison cannot be done herein. Moreover, as concluded by Knudsen et al. [66] and also reported by Lith et al. [24], at temperatures above 1000 °C, K and S release may become important and devolatilization of K_2SO_4 can take place, which results in low K and S content in the ash yield. A remarkable reduction in the amount of sulphur in SL ash collected from WMR (1040 °C) as compared to ashing furnace combustion (750 ºC), from 0.44 wt.% to 0.03 wt. %, was related to a significant emission of S around and above 1060 °C, as explained by Chinchon et al. [67]. Other elements in SL ash yield obtained from both methods were not affected by the different temperature of the methods used in this work.

Table 4.2 EDS elemental analysis (wt.%) of biomass and lignite ashes obtained from WMR and ashing furnace. Results are in oxygen and carbon free basis and are normalized in fuel basis.

	Ashes from WMR			Ashes from ashing furnace		
Temperature	1040 °C			575 °C for biomass, 750 °C for lignite		
Element	HS-A	OR-A	SL-A	HS-A	OR-A	SL-A
Na	-	0.09	0.17	0.01	0.16	0.17
Mg	0.1	0.17	0.19	0.09	0.15	0.2
Al	-	0.14	3.52	0.06	0.15	3.95
Si	0.1	0.32	5.83	0.13	0.31	6.16
P	0.1	0.25	0.05	0.07	0.22	0.04
S	-	0.05	0.03	0.05	0.13	0.44
Cl	-	0.01	-	-	0.22	-
K	0.3	0.99	0.49	0.71	2.36	0.42
Ca	0.4	0.65	1.19	0.56	0.63	0.9
Cr	0.3	0.09	-	-	-	-
Fe	0.1	0.13	1.08	0.05	0.17	0.82

4.2 Pyrolysis of Fuels

Volatile yield, char morphology, and char chemical kinetics from pyrolysis experiments were obtained under different operating parameters and are outlined in this subsection. The effect of parameters such as temperature, fuel type, and moisture is addressed and discussed. All fuel samples were pyrolyzed at 2200 ºC/s, and HS-A and HS-D were additionally pyrolyzed at 4500 ºC/s to investigate the effect of the heating rate. Trials were conducted under inert nitrogen atmosphere in a wire mesh reactor (WMR). According to preliminary pyrolysis experiments (see subsection 3.3.2, Figures 3.23 and 3.24), a residence time of 5 seconds was chosen for the pyrolysis of all fuels. Hazelnut shell (HS), Soma lignite (SL), and their two blends with mixture ratios of 50 wt.% SL – 50 wt.% HS and 75 wt.% - 25 wt.% HS were pyrolyzed. Volatile yields from WMR pyrolysis of individual and blended fuels were obtained from weighing the samples before and after each trial, and further compared with low heating rate (20 °C/min) proximate analysis results. Morphology of individual chars and respective blends was observed using SEM and BET surface area analysis was carried out to study effect of high heating rates on char surface areas. Char reactivities of individual and blended chars were evaluated through isothermal char oxidation experiments in TGA.

4.2.1 Volatile Yield

Apparent volatile yields were obtained for all fuels and blends at high (WMR) and low heating rates (TGA) and are presented in Figures 4.2 and 4.3.

WMR volatile yields from both as received and dried HS, showed higher values, ~85 wt. %, than proximate analysis (HS-A: 75 wt. %, HS-D: 79.5 wt.%). A similar trend was also observed in a work carried out by Trubetskaya et al. [35] who explained that, at high heating rates and elevated temperatures, enhanced devolatilization may cause high volatile yields in WMR. Moreover, as clarified by Trubetskaya et al. [37], pyrolysis in proximate analysis takes place at a low heating rate and maximum temperature of 950 ºC, which may reduce the volatile yield through secondary tar cracking. Based on a study carried out by Laurendeau [38], high volatile yield may also be due to the gasification of char-CO_2, since CO_2 is present in the reactor along with pyrolysis gases at temperatures (1100 ºC, 1550 ºC) above the temperature for char-CO_2 gasification (800 ºC). Similarly, in the study by Gil et al. [39], [40] char-CO_2 gasification was given as the reason for the high volatile yields from different biomass chars.

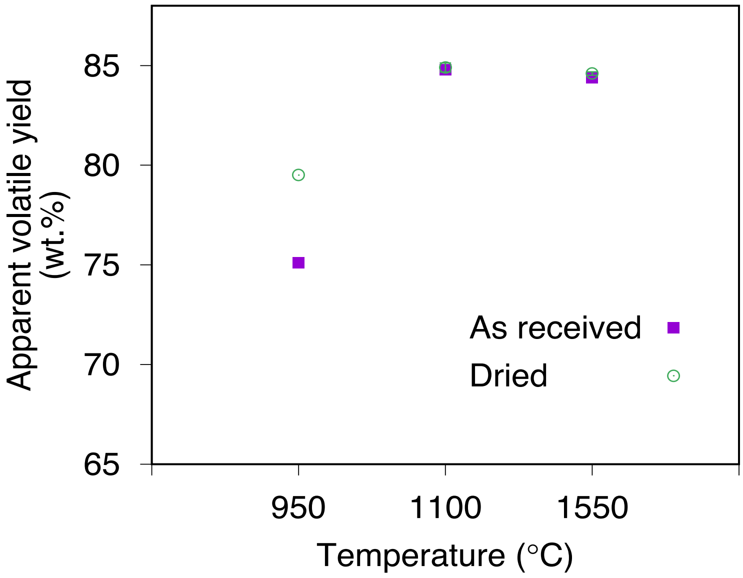

Figure 4.2 Volatile yield with respect to temperature for hazelnut shell pyrolysis at 2200 ºC/s and 4500 ºC/s and 5 s residence time. Vertical bars are depicted for WMR data points (1100 and 1550 ºC) and represent 98% confidence statistical error.

The volatile yields of individual chars and coal-biomass blend chars with two different mixing ratios, obtained from WMR pyrolysis tests at 1100 ºC are presented in Figure 4.3. In the figure, the volatile yields of as received (HS-A) and dried (HS-D) chars obtained from pyrolysis at WMR at 1100 ºC and 1550 ºC temperatures, as well as those from proximate analysis (PA) at 950 ºC for comparison purposes. The volatile yield of SL from WMR (37.3 wt.%) was close to the PA value (32.2 wt.%), while for HS yields were 75.1 wt.% from PA and 84.8 wt.% from WMR. Since HS had a lower ash content than SL (0.9 wt. % and 13 wt. %, respectively), hazelnut shell pyrolysis was characterized by a lower char yield, or conversely a higher volatile yield.

While the volatile yield from co-pyrolysis of 75 wt.% SL – 25 wt.% HS in WMR (44.2 wt.%) resembled that of PA (42.9 wt.%), the yields of the 50% blend (~51 wt. %) were lower for WMR as compared to PA (~54 wt. %). Since SL had a lower volatile matter than HS, as SL percentage increased in the blend, the volatile yield decreased. Furthermore, biomass components are bonded with weak ether linkages [68]. During thermal decomposition, these bonds in biomass decompose easily compared to coal which mainly consists of polycyclic aromatic hydrocarbons that have stronger bonds [68]. Therefore, HS had higher pyrolysis rate and volatile yield as compared to SL.

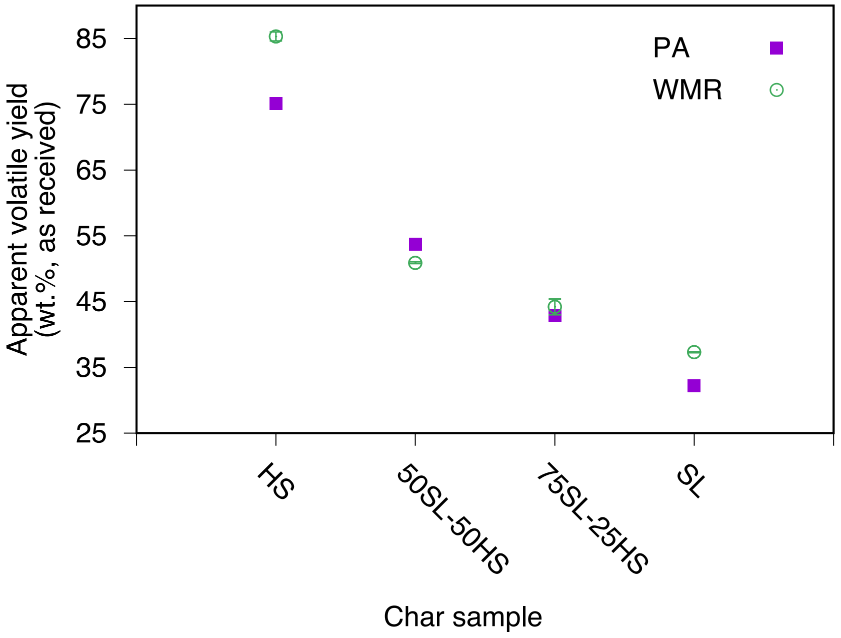

Figure 4.3 Apparent volatile yields of as received HS (HS-A), SL and their blends obtained from WMR pyrolysis at 1100 ºC for 5 seconds. PA – values from proximate analysis. Vertical bars in the WMR datapoints represent 98% confidence statistical error.

4.2.2 Char Morphology

Scanning Electron Microscopy (SEM) was used to study the morphology of the parent fuels and structural changes of the char samples obtained from fast pyrolysis at high temperatures (1100 ºC and 1550 ºC), high heating rates (2200 ºC/s and 4500 ºC/s), and short residence time (5 s). Figure 4.4 shows the SEM micrographs of dried and as received hazelnut shell chars (HS-D, HS-A) obtained from WMR pyrolysis experiments at two different heating rates, 2200 ºC/s and 4500 ºC/s.

In this study, due to the release of volatile matter during pyrolysis, chars with some meso/macro sized pores (Figure 4.4 b4, c4, d3, d4) but with low surface areas (Table 4.5) were obtained. The reason of low surface area was the rapid devolatilization at high heating rates, further evaluated by BET surface area analysis and discussed in subsection 4.2.4. Chars of as received and dried HS samples formed from WMR pyrolysis at 2200 ºC/s and 4500 ºC/s showed a non-uniform structure with smooth surfaces, rounded edges, and overall melted-like appearance. Agglomeration of particles was observed in the SEM images of chars, unlike the parent fuels (Figure 4.4. 2a, 2b, 2c, 2d, 2e). The reason of this agglomeration might be the melting of alkali metals such as potassium in hazelnut shell (cf. Table 4.3) at high pyrolysis temperatures (>2000 ºC) as stated by Yao et al. [69]. Melting of chars is a sign of plastic deformation and typically occurs under high heating rates [70]. SEM images in Fig 4.4. suggested that neither moisture content nor heating rate above 2200 ºC/s (specifically 4500 ºC/s) had a significant influence on char morphology.

HS, SL, and blends were pyrolyzed at a temperature of 1100 ºC and heating rate of 2200 °C/s to assess the effect of increasing biomass content on co-pyrolysis of HS with SL. The SEM images of individual chars, blended chars (50 SL-50 HS and 75 SL-25 HS), and as received HS and SL parent fuels are presented in Figure 4.5. Comparison of SEM images of HS-A parent fuel and its char from 1100 ºC WMR pyrolysis experiments showed clearly discernible particles in the parent fuel, whilst the char particles formed agglomerates. According to the study carried out by A. Trubetskaya [35], "due to catalytic effect of K and Ca, bridges may transform into char links resulting in polymerization which decreases char fluidity appearance." This suggestion was in accordance with the observed herein for HS char. Soma lignite (SL) chars showed similarity to SL parent fuel in terms of shape (both were angular), and a discrepancy in porosity (higher porosity of the char).

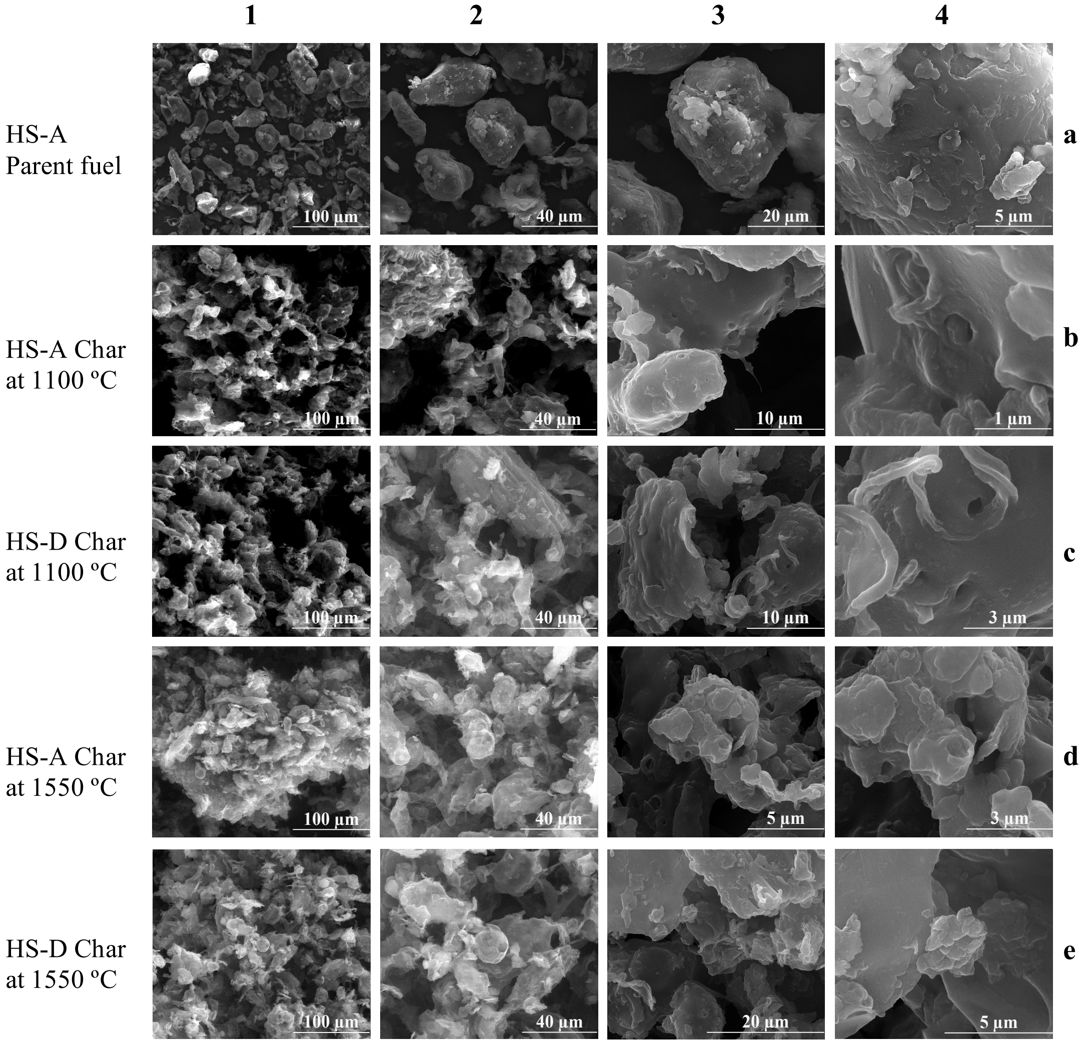

Figure 4.4 SEM images of hazelnut shell chars obtained from two different heating rate (2200 ºC/s and 4500 ºC/s) pyrolysis experiments (-A as received, -D dried fuel).

Blended char particles were either with smooth surfaces or with submicron particles scattered over the surface of large particles. Interactions between HS and SL in the blends were noticeable in the SEM images of the chars. As HS content increased in the blends, overlapped layers were observed in the 75 SL – 25 HS blend (see Figure 4.5 d2, d3, d4), and resulted in extensively melted chars with the increase in HS (50 SL – 50 HS, see Figure 4.5 c3, c4). Submicron particles over the 75 SL-25 HS blend chars were observed, which might be the effect of tar deposition [71] arising from rich content of alkaline metal (K), earth alkaline metal (Ca) in the ash of hazelnut shell (see Table 4.4).

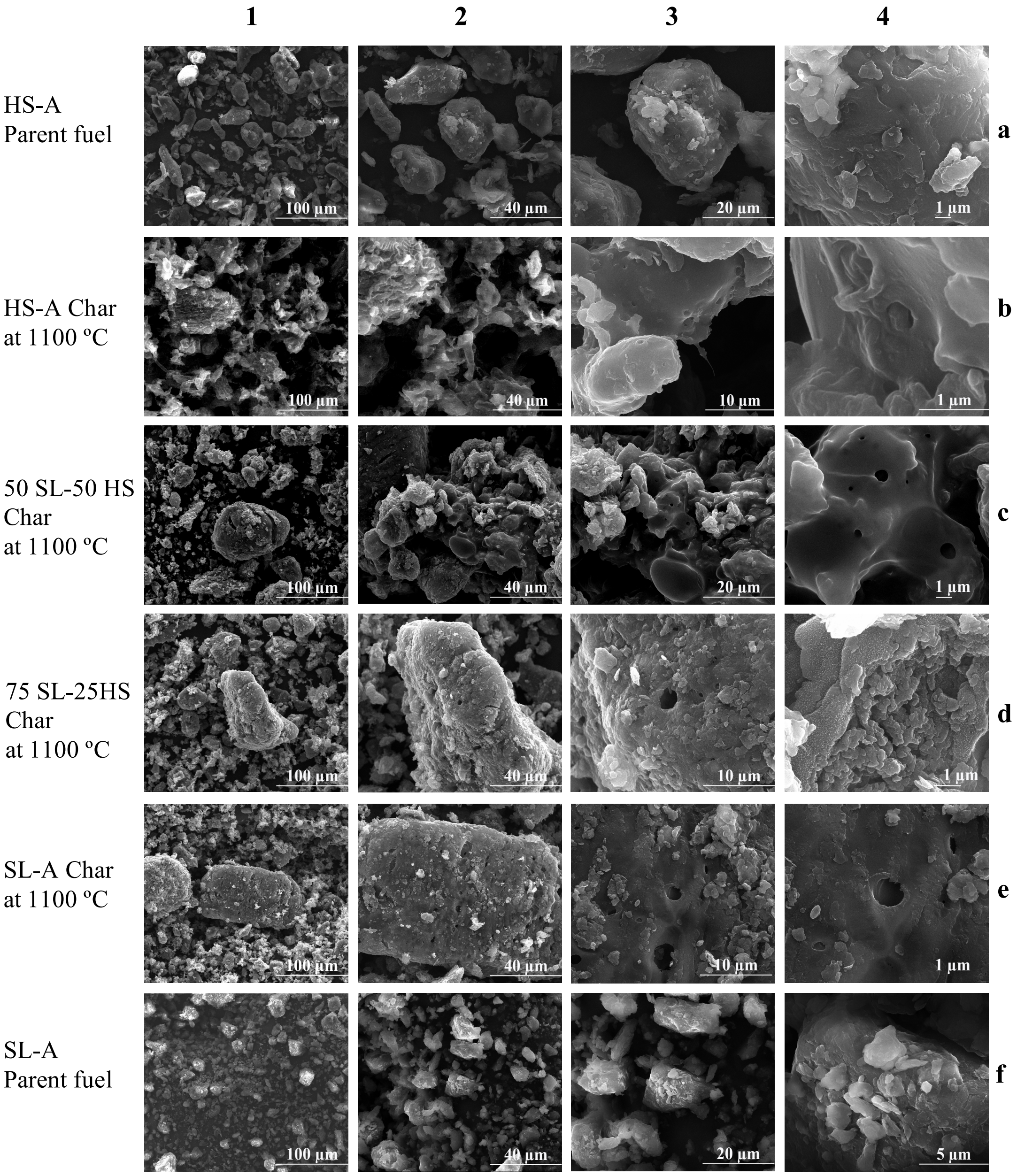

Figure 4.5 SEM images of as received hazelnut shell parent fuel, individual and blended chars obtained from 1100 ºC (2200 ºC/s) pyrolysis experiments (-A as received).

The formation of blow holes due to degassing was observed for several of the chars studied in the present work (see Figure 4.5 SL char (e4), 50% SL blend (c4) and 75% SL blend char (d3)). This was in line with previous observations by Fermoso [72] who studied the pyrolysis of low ranked coals at 1000 ºC. According to Zeng et al. [73], at high heating rate conditions the surface tension of bubbles is overcome, followed by blow up, which hinders swelling. Similarly, no swelling was observed in the obtained chars. Moreover, softening may occur in lignite pyrolysis and together with devolatilization, shrinkage in physical shapes of chars can be noticed [73]. Such blow hole structures (Figure 4.5 b4, c4, d3, d4, e3, e4) and shrinkages/contraction (Figure 4.5 c4) were observed in SEM images of chars from SL and blended fuel pyrolysis experiments in this study.

4.2.3 Char Chemical Composition

In order to study the effect of temperature and moisture on the chemical composition of HS char, EDS analysis was performed. EDS analysis results (in fuel basis) of as received and dried hazelnut shell chars obtained from both pyrolysis experiments (1100 ºC and 1550 ºC) are shown in Table 4.3. Potassium and calcium contents were the dominant elements in all hazelnut shell chars, while the Al and Si were present in low amount. No significant effect of temperature or moisture was observed in the chemical composition of all HS chars obtained from pyrolysis experiments conducted at either temperature (1100 ºC and 1550 ºC).

Table 4.3 EDS results (wt.%) of as received and dried hazelnut shell chars obtained from 1100 ºC and 1550 ºC pyrolysis experiments. Results are in fuel basis. (-A as received, -D dried)

	Chars from WMR pyrolysis			
Elements	1100 ºC HS-A	1100 ºC HS-D	1550 ºC HS-A	1550 ºC HS-D
Na	-	-	-	0.23
Mg	0.44	0.51	0.46	0.75
Al	0.27	0.38	0.2	0.38
Si	0.89	1.06	0.82	1.3
P	0.58	0.7	0.64	0.77
S	0.26	0.15	0.11	0.11
K	7.01	6.37	7.37	5.99
Ca	4.85	5.0	5.33	5.13
Fe	0.89	0.93	0.68	0.73

The chemical composition of the blended chars was also investigated using EDS. Table 4.4 show EDS analysis results of individual and blended chars in fuel basis. As Soma lignite (SL) percentage increased in the blends, Si, Al, and Fe increased, while K content decreased.

Table 4.4 EDS results (wt.%) of individual and blended chars from 1100 ºC pyrolysis experiments. Results are in fuel basis. (-A as received)

	Chars from WMR pyrolysis			
Elements	1100 ºC HS-A	1100 ºC 50 SL-50 HS	1100 ºC 75 SL-25 HS	1100 ºC SL-A
Na	-	0.45	0.44	1.39
Mg	0.44	0.64	0.69	0.95
Al	0.27	8.05	9.04	14.45
Si	0.89	11.9	13.6	22.93
P	0.58	0.27	0.37	-
S	0.26	1.49	1.93	3.30
K	7.01	2.51	3.26	1.49
Ca	4.85	3.36	5.38	3.38
Fe	0.89	2.78	3.39	4.11

4.2.4 BET Surface Area Analysis of the Chars

Using Brunauer–Emmitt–Teller (BET) analysis through nitrogen adsorption at 77 K surface areas of all fuels were studied. Results for HS parent fuel and char samples pyrolyzed at 1100 ºC and 1550 ºC, in as received and dried form are shown below in Table 4.5, and for all remaining chars in Table 4.6.

Table 4.5 BET Surface areas of as received hazelnut shell parent fuel and as received, dried hazelnut shell chars obtained from WMR pyrolysis at 1100 ºC and 1550 ºC temperatures.

Chars and parent fuel	BET Surface area (m^2/g)
HS-A parent fuel	2.9
1100 ºC HS-A char	15.1
1100 ºC HS-D char	22.9
1550 ºC HS-A char	14.6
1550 ºC HS-D char	7.8

In accordance to literature [74], [75], [76], [77], [70] BET surface areas of biochars obtained at high heating rates presented high values (95-275 m^2/g). However, in some studies [22], [74], [78], [79] chars with low surface areas (0.7-6 m^2/g) were also obtained. In the present work, low char surface areas in the order of 15 m^2/g were measured from BET surface analysis. As concluded by Zhai et al. [42], during high heating rate pyrolysis fast release of large amount of volatiles creates macropores with subsequent crash of micropores. As a consequence, char surface areas may decrease. Similarly, in the present study, low surface areas with mesopores were observed in all HS chars obtained at high heating rates (~2200 ºC/s and 4500 ºC/s).

The effect of temperature on char BET surface area was not monotonous for HS-A and HS-D. On the one hand, BET surface areas of as received (A) hazelnut shell chars were same (15 m^2/g) at two different pyrolysis temperatures (1100 ºC, 1550 ºC), which was related with the similar volatile yields presented by these fuels (see Figure 4.2). While on the other hand, surface areas of the chars obtained from dried fuels were affected by different pyrolysis temperatures, which was not in line with the similar volatile yields of these fuels (see Figure 4.2).

In this study, the effect of moisture was dependent on the temperature during WMR pyrolysis. As received HS chars obtained at 1550 ºC had higher surface area, 14.6 m^2/g, than dried hazelnut shell chars which was 7.8 m^2/g. However, a reverse trend was observed in the chars formed at 1100 ºC pyrolysis temperature (HS-D: 22.9 m^2/g, HS-A: 15.1 m^2/g). Demirbaş et al. [14] studied the effect of moisture on surface areas of the chars formed at elevated pyrolysis temperatures. According to their study, the surface area of chars obtained from fuels with high water content are larger due to the pores formed upon moisture release.

Table 4.6 shows the BET surface area and pore size results of parent fuel HS and SL, individual chars of HS and SL, and blended chars. All chars were obtained at 1100 ºC in the WMR. The surface area of SL char was larger than HS char, 28.2 m^2/g vs 15.1 m^2/g. Since HS had higher volatile yield (75.1 wt.%) than SL (32.2 wt.%), the rapid release of volatiles at high heating rate pyrolysis resulted in chars with lower surface areas which was attributed to the crash of micropores and formation of macropores as aforementioned. SL chars presented higher surface area (28.2 m^2/g) than the parent SL (8.7 m^2/g). This nearly threefold increase was due to high heating rate pyrolysis condition [80], as observed by Çakal et al. [81] who pyrolyzed Soma lignite (SL) at 1000 ºC.

Table 4.6 BET Surface areas and pore sizes of parent fuel and individual and blended chars obtained from WMR pyrolysis at 1100 ºC.

Char and parent fuels	BET Surface areas (m^2/g)	Pore size (nm)
1100 ºC SL-A char	28.2	2.00
1100 ºC 75% SL blend char	14.4	2.40
1100 ºC 50% SL blend char	44.7	2.40
1100 ºC HS-A char	15.1	2.40
SL-A parent fuel	8.7	2.40
HS-A parent fuel	2.9	3.00

The pore size of HS and SL for parent fuel, char, and char blend forms was also obtained and is presented in Table 4.6. BET analysis allows quantification of mesopores (2<d<50 nm) and macropores (d>50 nm) [19]. However, micropores cannot be determined from BET analysis. According to Burhenne et al [82], micropores do not influence char combustion because of diffusion limitations which was also reported by Kazanç et al. [22], therefore in this study no particular emphasis to microporosity of the chars was given. Pore sizes of parent fuels, individual and blended chars were similar and within mesoporous size category. Pore diameters were similar to all studied fuels and approximately equal to 2.5 nm.

4.2.5 Char Chemical Kinetic Analysis

In the scope of this work, the burnout extent, burnout time, rate of burnout, and first order rate constants of all chars obtained from WMR trials at 1100 ºC, 1550 ºC were studied. The aforementioned parameters were calculated using the data from TGA isothermal tests. In isothermal char combustion, it is important to have kinetically controlled regime, Regime I, which diminishes heat and mass transfer limitations [83]. Therefore, for biochars, preliminary studies were carried out at three different temperatures (400 °C, 450 °C, 500 °C) in order to decide on appropriate isothermal temperatures for char-air combustion (see Fig. 4.7). Temperatures of 400 °C for HS and 450 ºC for SL and blends were chosen. Figure 4.6 shows three different carbon burnout profiles of as received hazelnut shell (HS-A) chars obtained from fast pyrolysis in WMR at 1100 °C. It is clear from Figure 4.6 that as isothermal combustion temperature increased, the reactivity of the chars also increased, and therefore, the required reaction time for a given burnout decreased (i.e. at 60 wt.% of carbon burnout, reaction time of around 5 min, 1.5 min, 1 min for 400 °C, 450 °C, 500 °C respectively). Burnout times are shown in Table 4.7. Both 90% and 100% burnout times are reduced significantly when moving from 400 to 450 ºC. At higher temperatures, e.g. 500 °C, the decrease of the reaction time appeared less important, in accordance with the results obtained by Morin et al. [83].

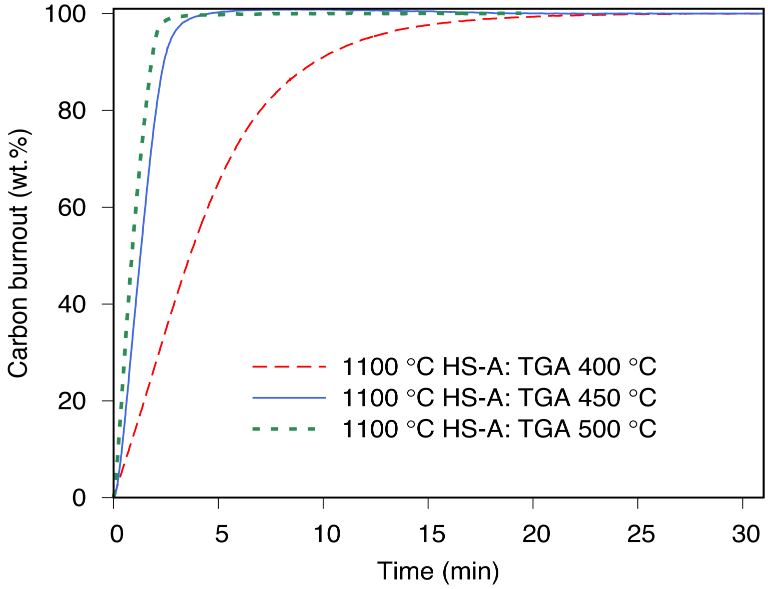

Figure 4.6 Carbon burnout as a function of time for as received hazelnut shell (HS-A) chars

Table 4.7 90 % and 100 % burnout times of as received hazelnut shell (HS-A) char obtained from 1100 °C pyrolysis at WMR.

Fuel	Time to 90% burnout (min)	Burnout time (min)
1100 °C HS-A TGA:400°C	9.60	31.0
1100 °C HS-A TGA:450°C	2.41	4.55
1100 °C HS-A TGA:500°C	1.82	7.60

Figure 4.7 presents carbon burnout rate as a function of carbon burnout of as received hazelnut shell chars obtained from 1100 °C pyrolysis at WMR. Each curve shows the burnout rate profile of HS-A char conducted at different isothermal combustion temperatures (400 °C, 450 °C, and 500 °C). For all three HS-A chars, the maximum rate of burnout was obtained at close burnout levels of 20 wt.%, 23 wt.%

and 25 wt.% respectively, which can be due to very similar char composition (see Table 4.3: EDS results).

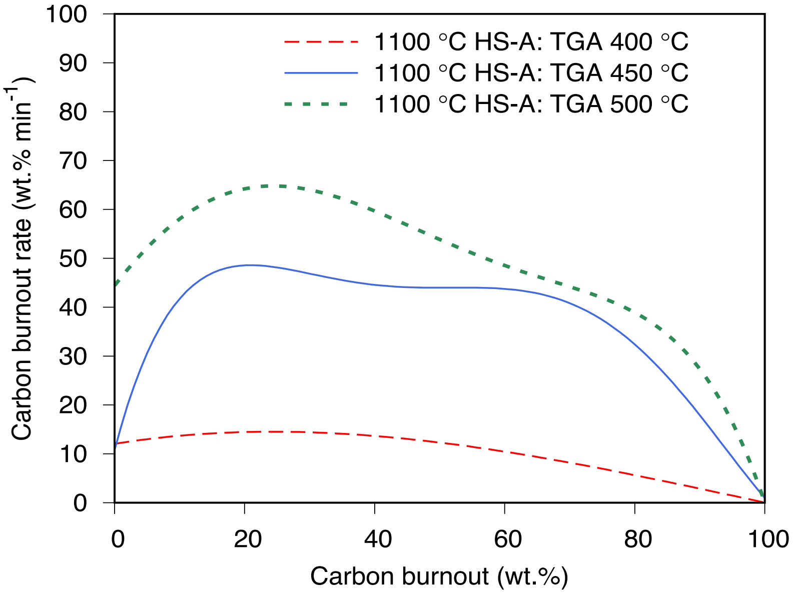

Figure 4.7 Carbon burnout rate as a function of burnout for as received hazelnut shell (HS-A) chars (experimental values). Polynomial fitted curves are of degree-3 for the results from TGA 400 °C and degree-5 for TGA 450 °C and 500 °C.

The carbon burnout profiles of HS-A, SL-A and blended char samples obtained from pyrolysis at 1100 °C at WMR are displayed in Figure 4.8. Isothermal oxidation of HS-A char samples was conducted at 400 °C, and at 450 ºC for SL-A and blended chars.

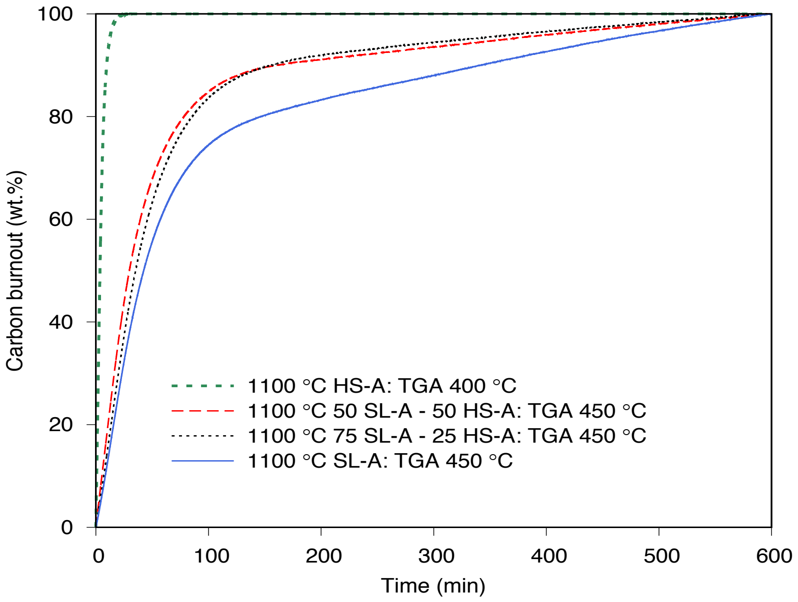

Figure 4.8 Carbon burnout profiles as a function of time for as received hazelnut shell (HS-A), lignite and blended char samples obtained from 1100 °C WMR pyrolysis.

It is clear from Fig. 4.8 that HS-A char, which required a very short time to reach 100 wt.% carbon burnout, had a higher reactivity than the SL-A and blended chars. As lignite percentage increased in the blended mixture, blended char burnout curves resembled SL-A char burnout curve. High reactivity of biomass chars compared to lignite and blended chars was related to the high alkaline content of biomass chars (see Table 4.4), which had a catalytic effect [79], [84].

Carbon burnout rate profiles of HS-A, SL-A, and blended chars are shown in Fig. 4.9. Maximum carbon burnout rates for biomass and lignite chars reached at burnout levels of 31 wt.% and 7.4 wt.% respectively. Lignite and blended chars showed almost six times lower maximum reactivity (1-2 wt.% min^{-1}) than the one from biomass char (~12 wt.% min^{-1}).

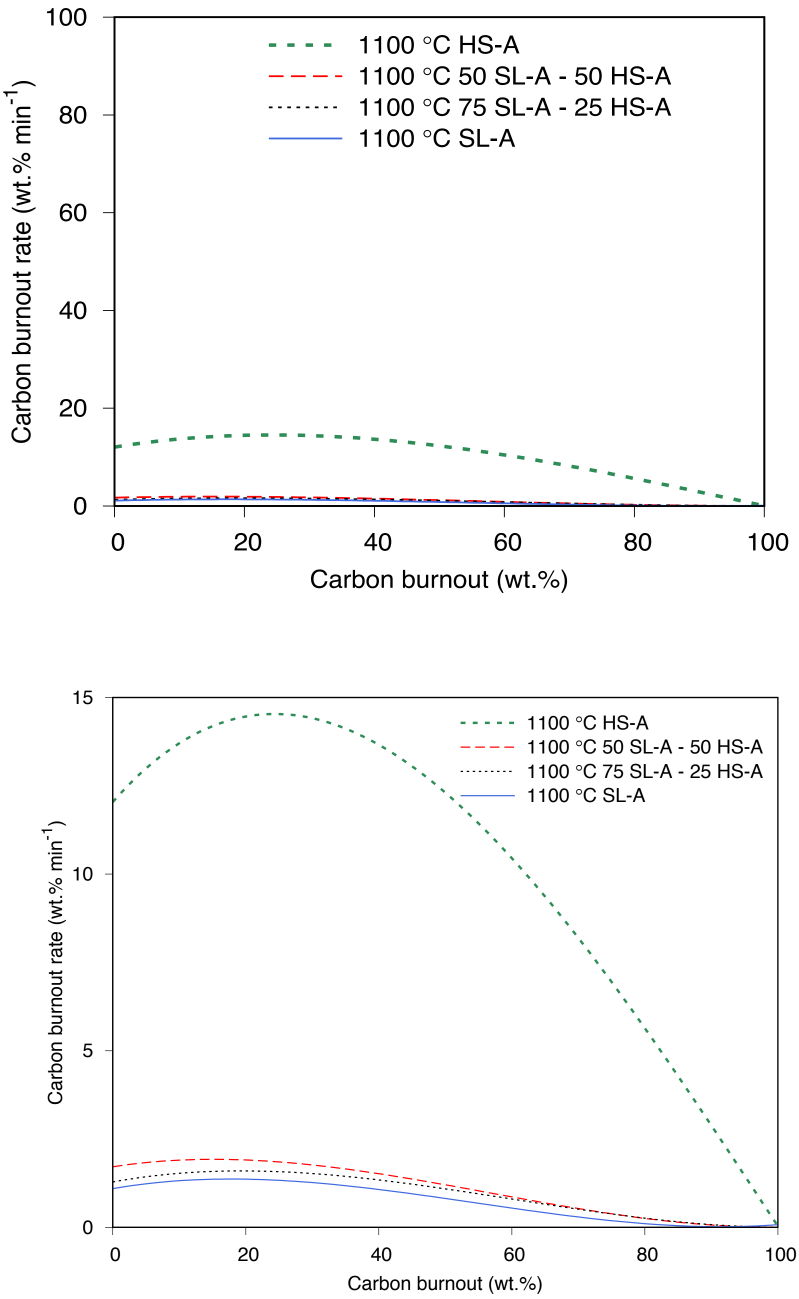

Figure 4.9 Carbon burnout rate as a function of burnout for as received hazelnut shell (HS-A) chars (experimental values). Polynomial fitted curves are of degree-3. Second plot is a magnified one.

To add more, as discussed by Kazanç et al. [22], one reason of having low burnout rates of lignite and blended chars than biomass char may be due to more stable compounds of coal. According to Wornat et al. [33], carbon bonds in biomass are dominantly aliphatic which can easily be broken, contrary to aromatic carbon bonds in coal chars.

Figure 4.10 shows the carbon burnout profiles of individual and blended chars obtained from 1100 °C pyrolysis experiments at WMR along with the predicted values. Predicted burnout values were obtained from the weighted sum related to corresponding profile of each individual char [19]. Isothermal TGA tests for HS-A char samples were conducted at 400 °C, while for SL-A and blended chars at 450 °C. In both predicted blends 50:50 and 75:25, SL char contribution was high, 80.5 wt.% and 92.5 wt.%, respectively. Therefore, the predicted profiles for the blends matched the SL profile very closely. However, experimental profiles for blends did not match SL profile which can be due to a synergy in co-pyrolysis of coal and biomass.

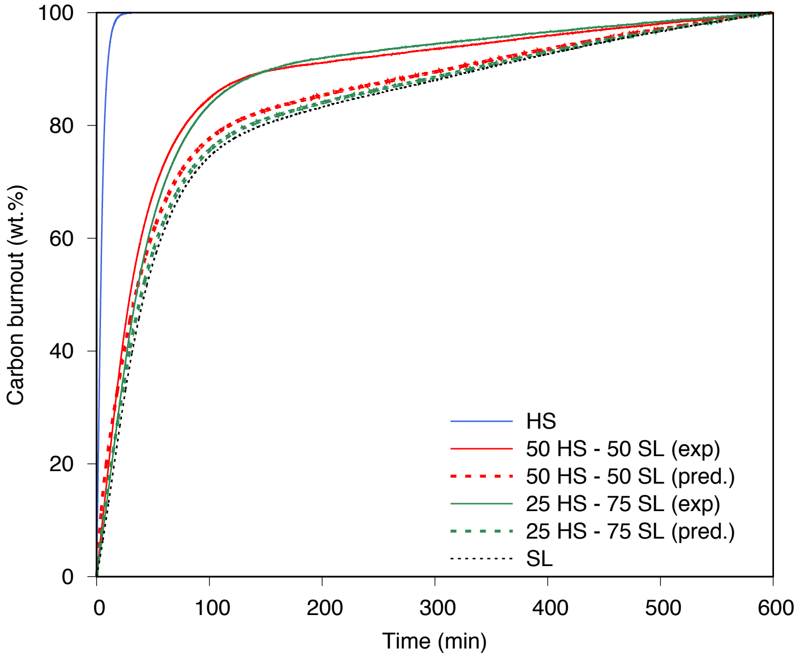

Figure 4.10 Carbon burnout profiles as a function of time of individual and blended chars. Experimental and predicted values of blended chars are given for comparison.

Table 4.8 shows time to 90 % and 100 % burnout of individual and blended chars for both experimental and predicted values. A significant difference was observed between experimental and predicted burnout profiles of 50:50 and 75:25 blends. Times required for 90 % of burnout for the predicted profiles of the blends, 50:50 and 75:25, (312 min and 332 min respectively) were much longer than those from experimental blend profiles (50:50 and 75:25) by nearly two-fold (161.4 min and 155.3 min respectively) (Table 4.8). The increase in SL had a reactivity decreasing effect, while the increase in HS had a reactivity enhancing effect (see Figure 4.10). Therefore, as lignite content increased, the time to reach 90 % of char burnout also increased.

As reported by Zhou et al. [85], chars with larger surface area and porous structure show higher reactivity. Similarly, in the present study, among the lignite and blended chars, 50SL:50HS blends which had 44.7 m^2/g of surface area (Table 4.6), showed higher reactivity (see Fig. 4.9) which was also due to high alkali metal content of biomass.

Comparison of experimental and predicted (i.e. additive) values for the blends display clear synergistic effects. As visible from Figure 4.10 and Table 4.8, the burnout times were lower for the experimental blends (both 50-50 and 75-25) as compared to the respective predicted values. Results from the study carried out by Zhang et al. [30], showed a similar trend as in the present study. In their study, in higher blending ratios more notably synergetic effect was observed. It was explained by that fact that, in blends with sufficiently high amount of biomass, higher hydrogen release results in hydrogenation effect on coal pyrolysis thereby increasing the synergistic effect [30].

Table 4.8 90 % and 100 % burnout times of individual and blended chars obtained from 1100 °C pyrolysis at WMR. TGA analysis for HS-A char carried out at 400 °C, while for lignite and blended chars at 450 °C.

Fuel	Time to 90% burnout (min)	Burnout time (min)
Individual chars		
HS-A	9.600	31.00
SL-A	342.0	598.7
Experimental values		
50 HS - 50 SL	161.4	598.0
25 HS - 75 SL	155.3	598.0
Predicted values		
50 HS - 50 SL	312.0	598.0
25 HS - 75 SL	332.0	598.0

In order to understand the effect of temperature and moisture on char reactivity, as received and dried hazelnut shell samples were additionally pyrolyzed at 1100 °C and 1550 °C temperatures in the WMR. Obtained chars were subjected to isothermal oxidation tests at 400 °C by using TGA (see Figure 4.11). The comparison of carbon burnout profiles showed that HS-D chars obtained at high heating rates were more reactive. At high heating rate pyrolysis conditions, volatiles were released rapidly, which in turn increases char reactivity [86]. Among the char samples in Figure 4.11, dried hazelnut shell (HS-D) char obtained at 1550 °C was the most reactive, while as received hazelnut shell (HS-A) char obtained at the same condition was the least. It was observed that char obtained from the wet fuel (1100 °C HS-A) at the lower heating rate in WMR (2200 °C/s), showed higher reactivity than the char obtained from the dried fuel (1100 °C HS-D). A reverse trend was seen in chars from pyrolysis at heating rate of 4500 °C/s, where the dried fuel chars (HS-D) from 1550 °C was more reactive than as received fuel chars (HS-A) obtained at the same condition.

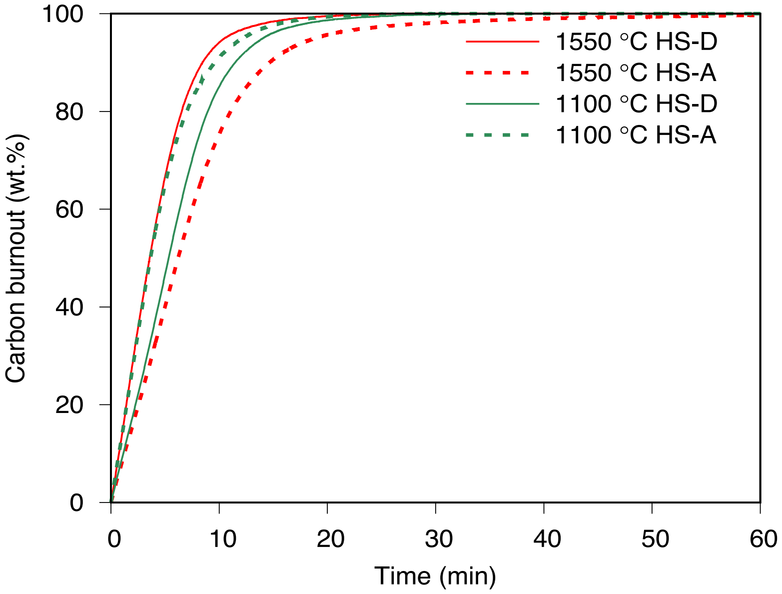

Figure 4.11 Carbon burnout profiles as a function of time for as received and dried hazelnut shell (HS-A, HS-D) char samples obtained from 1100 °C and 1550 °C WMR pyrolysis.

Maximum reactivities (Fig. 4.12) of as received and dried chars obtained from 1100 °C and 1550 °C pyrolysis experiments, showed almost similar results (9-13 wt.% min^{-1}) which can be attributed to the similar alkali and earth alkaline metal contents (K, Ca, Mg) of the chars (see Table 4.3). Dried hazelnut shell chars from 1550 °C pyrolysis and as received hazelnut shell chars from 1100 °C pyrolysis showed similar and the highest carbon burnout rates of approximately 13 wt. %/min^{-1}. Maximum carbon burnout rates for HS-D (1550 °C), HS-A (1550 °C) and HS-A (1100 °C) were reached at burnout levels of 20-25 wt.%, however, for HS-D (1100 °C), it was reached at a burnout of ~50 wt.%. It was concluded that moisture had no significant effect on char reactivity.

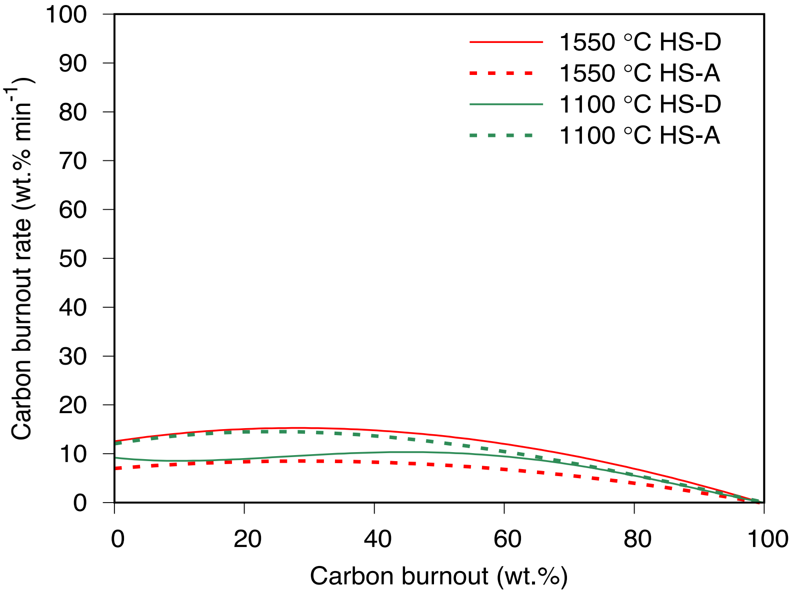

Figure 4.12 Carbon burnout rate as a function of burnout for as received and dried hazelnut shell (HS-A) chars (experimental values) obtained from WMR pyrolysis at 1100 °C and 1550 °C. Polynomial fitted curves are of degree-3 for 1550 °C HS-D, 1550 °C HS-A, 1100 °C HS-A and degree-4 for 1100 °C HS-D curves.

Table 4.9 presents apparent first order rate constants and R^2 values of experimental and predicted curves of individual and blended chars. As aforementioned, isothermal char oxidation of hazelnut shell (HS) chars was conducted at 400 °C while, and at 450 ºC for Soma lignite (SL) and blended chars.

Among the individual chars, reaction rate constant of HS chars was the highest with 0.0043 min^{-1}, while the one for SL chars was lower at 0.00009 min^{-1}. The reason of high rate constant value of hazelnut shell (HS) chars compared to SL chars, can be associated with aliphatic bonds in biomass which are broken easily than aromatic C-N bonds present in lignite chars [33]. To add more, due to high content of catalytic element, K, in hazelnut shell chars (see Figure 4.4) which made them more reactive, resulted in higher first order rate constant of HS chars than SL char [38], [79]. Comparison of experimental rate constants of 50-50 and 75-25 blends showed no difference since they had a similar chemical composition (see Figure 4.4). Nonetheless, experimental values were higher than the predicted, which can be explained as synergetic effect of SL and HS co-pyrolysis. The reason of such a low rate constant for SL was the long isothermal char combustion time, 600 min. For a comparison purpose, SL char was also burned isothermally at 450 °C for 120 min, where the rate constant was higher, 0.0005 min^{-1}, still lower than the one from HS char in one order of magnitude.

Table 4.9 First order kinetic rate constants of hazelnut shell (HS), Soma lignite (SL) and blended chars determined from experimental and predicted curves.

Parameters Fuel	1st order rate constant (min^{-1})	R^2
Individual chars		
1100 °C HS-A 400 °C-120 min	0.0043	0.99688
1100 °C SL-A 450 °C-600 min	0.00009	0.93827
1100 °C SL-A 450 °C-120 min	0.0005	0.99126
Experimental values		
50 HS - 50 SL-600 min	0.0001	0.84062
25 HS - 75 SL-600 min	0.0001	0.88110
25 HS - 75 SL-120 min	0.0005	0.99275
Predicted values		
50 HS - 50 SL	0.00009	0.92622
25 HS - 75 SL	0.00008	0.93373

In Table 4.10, reaction rate constants and R^2 values of dried and as received hazelnut shell (HS-D, HS-A) chars obtained at 1100 °C and 1550 °C pyrolysis experiments are showed. Isothermal char combustion experiments of hazelnut shell (HS) chars were performed in TGA at 400 °C. The highest reaction rate constant (0.0051 min^{-1}) was observed for the dried hazelnut shell (HS-D) chars obtained at 1550 °C pyrolysis. According to Huang et al. [87], melting temperature of alkali carbonates, Li_2CO_3, Na_2CO_3, K_2CO_3, is around 900 °C, which enhances rate of heat transfer when the dissociation of potassium carbonates starts to takes place at 1300 °C [22]. To add more, the dissociation of $CaCO_3$ at 900 °C [60], plays catalytic effect on oxidation reactions [22], [38].

Table 4.10 First order kinetic rate constants of dried and as received hazelnut shell (HS-D, HS-A) chars obtained at 1100 °C and 1550 °C pyrolysis experiments. Chars were isothermally burned in TGA at 400 °C.

Parameters / **Fuel**	**1st order rate constant (min^{-1})**	**R^2**
1550 °C HS-D	0.0051	0.98959
1550 °C HS-A	0.0029	0.99352
1100 °C HS-D	0.0038	0.98322
1100 °C HS-A	0.0043	0.99782

CHAPTER 5

CONCLUSION AND FUTURE RESEARCH

5.1 Conclusion

In this study, novel wire mesh reactor (WMR) was used to study combustion and fast pyrolysis of Turkish biomass and lignite fuels namely, hazelnut shell (HS), olive residue (OR) and Soma lignite (SL) at high temperature (~ 1300 °C) and at high heating rates (~ 3000 °C/s). Isothermal thermogravimetric analysis (TGA) was performed to investigate char oxidation. Bio-chars were burned isothermally at 400 °C while lignite (SL) and blended chars, 50 wt.% SL – 50 wt.% HS and 75 wt.% - 25 wt.% HS, at 450 °C. Conclusions are summarized below:

- Ash yields from hazelnut Shell (HS) and Soma lignite (SL) obtained from high heating rate combustion (1015 °C/s) in WMR and low heating rate combustion in ashing furnace and proximate analysis showed close values.
- Ash yield from olive residue (OR) seemed to be affected by high temperature (1040 °C) combustion in WMR. Almost 1.5 times less ash yield was obtained from WMR combustion than ashing furnace and proximate analysis. Decrease was due to a marked loss of K, which was related to a rapid evaporation of potassium oxide (K_2O) above 900 °C. Furthermore, a significant reduction in the concentration of Cl and S was also observed. Deacrease of Cl can be attributed to KCl sublimation at high combustion temperatures, while decrease in S content could be due to devolatilization of alkali metal sulfates like K_2SO_4 at temperatures above 1000 °C.
- A trace element of Cr was observed in hazelnut shell ash obtained from 1040 °C combustion in WMR. Due to high alkali content of biomass, oxidized Cr (III) may deposit on the surface of ash particles.

- A remarkable reduction in the amount of Sulphur in SL ash collected from 1040 °C combustion was observed which was related to significant amount of S emission around and above 1060 °C.
- Volatile yields from pyrolysis of both dried and as received hazelnut shell fuels at 2200 C/s and 4500 C/s in WMR, showed high volatile yields around 85 wt.% than low heating rate (20 C/min) proximate analysis, 75 wt.%. This effect was explained to be due to enhanced devolatilization at elevated temperatures (1100 °C, 1550 °C) and high heating rates (2200 °C/s, 4500 °C/s). Moreover, high volatile yield at high temperature (1100 °C, 1550 °C) conditions may also be originated from gasification of char-CO_2, which requires a minimum temperature of 800 °C to gasify. To add more, since the lignin, cellulose and hemicellulose bonded together with weak ether linkages, their decomposition becomes easier during thermal decomposition.
- Volatile yield for Soma lignite (SL), 37.3 wt.% was close to the one from proximate analysis (PA), 32.3. wt.%. For blended fuels, volatile yield increased as lignite content decreased. Since coal consists of polycyclic aromatic hydrocarbons, their decomposition during thermal decomposition becomes harder.
- Agglomeration of particles in SEM images of as received and dried hazelnut shell chars was observed which was originated from melting of alkali metals like, K, at high pyrolysis temperatures (1100 °C, 1550 °C). This melting phenomenon is also known as plastic deformation which takes place at high heating rates.
- No significant influence of moisture on as received and dried hazelnut shell (HS-A, HS-D) char morphologies obtained at high heating rates (2200 °C/s, 4500 °C/s) was observed.
- BET surface areas of the chars were characterized by being low, and was due to rapid devolatilizaiton during high heating rate pyrolysis where the micropores were collapsed and macropores were formed.

- SL chars presented higher surface area (28.2 m^2/g) than parent SL fuel (8.7 m^2/g) nearly threefold increase was observed which was due to the growth of coal micropores.
- Chars with larger surface area and porous structure show higher reactivity. among the lignite and blended chars, 50SL:50HS blends which had 44.7 m^2/g of surface area showed higher reactivity.
- Biomass chars showed the highest reactivity due to high content of alkali metals, which has a catalytic effect.
- Synergetic effect was observed in co-pyrolysis of SL and HS. Higher blending ratios of lignite and coal like in, 50 wt.% SL – 50 wt.% HS, showed higher reactivity which was due to high amount of hydrogen release from sufficiently high content of biomass which showed hydrogenation effect on coal pyrolysis and increased synergetic effect

5.2 Future Research

Based on the results obtained from this study and according to the researches carried out in literature, following further research studies were decided to be performed.

- It is aimed to perform pyrolysis experiments of Turkish fuels in an inert Nitrogen environment where continuously sweeping Nitrogen gas is introduced to the system in order to remove released volatile matter and to prevent their deposition onto the mesh.
- Gas collection part in the wire mesh system which was not utilized in the present study, is aimed to be developed and to be used in order to study released pyrolysis gases by using gas chromatography.
- In order to study effect of pressure on pyrolysis of the fuels, it is planned to carry out pyrolysis experiments at the vacuum and at different pressure conditions.

- In this work, single layer combustion of the selected fuels was studied in wire mesh reactor (WMR). Wire mesh system shown in the present study, has also a single particle arrangement, where the mesh is held in a vertical position. Such arrangement, enables to study a single particle combustion in wire mesh reactor in order to investigate particle ignition behavior. To do so, a high-speed camera will be utilized to record the thermal decomposition process from an optical access window which is in top of the chamber in the wire mesh system.

REFERENCES

[1] Republic of Turkey Energy Market Regulatory Authority , "Electricity Market Development Report," Ankara, 2016.

[2] T.C. Enerji Ve Tabii Kaynaklar Bakanlığı, "Biyokütle," [Online]. Available: http://www.enerji.gov.tr/tr-TR/Sayfalar/Biyokutle. [Accessed 25 July 2018].

[3] Toprak Mahsülleri Ofisi, "Report of hazelnut sector," Turkish Grain Board, 2016.

[4] A. Demirbaş, *Calculation of higher heating values of biomass fuels,* Fuel, 1997, pp. 431-434.

[5] M. Flower and J. Gibbins, "A radiant heating wire mesh single-particle biomass combustion apparatus," *Fuel,* vol. 88, pp. 2418-2427, 2009.

[6] J. Riaza, J. Gibbins and H. Chalmers, *Ignition and combustion of single particle of coal and biomass,* vol. 202, Fuel, 2017, pp. 650-655.

[7] R. Loison and R. Chauvin, "Pyrolyse rapide du charbon," vol. 91, no. 3, pp. 269-275, 1964.

[8] L. Gao, L. Wu, N. Paterson, D. Dugwell and R. Kandiyoti, "The use of wire mesh reactors to characterise solid fuels and provide improved understanding of larger scale thermochemical processes scale thermochemical processes," *Int. J. Oil, Gas and Coal Technology,* vol. 1, no. 1/2, pp. 152-179, 2008.

[9] S. van Loo and J. Koppejan, The Handbook of Biomass Combustion and Co-firing, London: Earthscan, 2008, pp. 1, 249, 250.

[10] M. Sami, K. Annamalai and M. Wooldridge, "Co-firing of coal and biomass fuel blends," *Progress in Energy and Combustion Science,* vol. 27, pp. 171-214, 2001.

[11] A. Trubetskaya, *Fast pyrolysis of biomass at high temperatures. PhD Thesis,* Department of Chemical and Biochemical Engineering.Technical University of Denmark, 2016.

[12] W.-H. Chen, J. Peng and X. T. Bi, "A state-of-the-art review of biomass torrefaction, densification and applications," *Renewable and Sustainable Energy Reviews,* vol. 44, pp. 847-866, 2015.

[13] A. Demirbas, Biohydrogen, London: Springer, 2009.

[14] A. Demirbas, "Combustion characteristics of different biomass fuels," *Progress in Energy and Combustion Science,* vol. 30, pp. 219-230, 2004.

[15] Robert C. Brown, Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power, First Edition ed., John Wiley & Sons, Ltd., 2011.

[16] S. G. Allen, L. C. Kam, A. J. Zemann and M. J. Antal, "Fractionation of Sugar Cane with Hot, Compressed, Liquid Water," *Ind. Eng. Chem,* vol. 35, pp. 2709-2715, 1996.

[17] C. Gokcol, B. Dursun, B. Alboyaci and E. Sunan, "Importance of biomass energy as alternative to other sources in Turkey," *Energy Policy,* vol. 37, pp. 424-431, 2009.

[18] A. Demirbas, "Fuel Characteristics of Olive Husk and Walnut, Hazelnut, Sunflower, and Almond Shells," *Energy Sources,* vol. 24, pp. 215-221, 2002.

[19] D. Magalhaes, F. Kazanç, A. Ferreira and M. Rabaçal, "Ignition behavior of Turkish biomass and lignite fuels at low and high heating rates," *Fuel,* vol. 207, pp. 154-164, 2017.

[20] N. S. Yuzbasi and N. Selçuk, "Air and oxy-fuel combustion characteristics of biomass/lignite blends in TGA-FTIR," *Fuel Processing Technology,* Vols. 1101-1108, p. 92, 2011.

[21] N. P. Gürkan, *Turkish Olive And Olive Oil Sectoral Innovation System: A Functional - Structural Analysis. PhD Thesis.,* The Programme Of Science And Technology Policy Studies. Middle East Technical University, 2015.

[22] F. Kazanç, D. Magalhaes and J. Riaza, "A study on the reactivity of various chars from Turkish fuels obtained at high heating rates," *Submitted to Fuel Processing Technology,* June 2018.

[23] R. C. Neavel, "Coal Structure and Coal Science: Overview and Recommendation," pp. 73-82.

[24] S. C. van Lith, P. A. Jensen, F. J. Frandsen and P. Glarborg, "Release to the Gas Phase of Inorganic Elements during Wood Combustion. Part 2: Influence of Fuel Composition," *Energy & Fuels,* vol. 22, pp. 1598-1609, 2008.

[25] S. V. Vassilev, K. Kitano and C. G. Vassileva, "Some relationships between coal rank and chemical and mineral composition," *Fuel,* vol. 75, pp. 1537-1542, 1996.

[26] S. F. Miller and H. H. Schobert, "Effect of the Occurrence and Composition of Silicate and Aluminosilicate Compounds on Ash Formation in Pilot-Scale Combustion of Pulverized Coal and Coal-Water Slurry Fuels," *Energy & Fuels,* vol. 8, pp. 1197-1207, 1994.

[27] M. Mando, "Direct combustion of biomass," in *Biomass combustion science, technology and engineering*, L. Rosendahl, Ed., Woodhead, 2013, pp. 61-83.

[28] D. Magalhaes, F. Kazanç, J. Riaza, S. Erensoy, Ö. Kabaklı and H. Chalmers, "Combustion of Turkish lignites and olive residue: Experiments and kinetic modelling," *Fuel,* vol. 203, pp. 868-876, 2017.

[29] H. Liu and B. H. Gibbs, "The significance of reburning coal rank on the reduction of NO in drop tube furnace.," in *International Symposium on Transport phenomena in combustion,*, San Francisco, CA, 1995.

[30] L. Zhang, S. Xu, W. Zhao and S. Liu, "Co-pyrolysis of biomass and coal in a free fall reactor," *Fuel,* vol. 86, pp. 353-359, 2007.

[31] O. Karlström, *Drying, devolatilization&char oxidation of solid fuel,* Abo Akademi 2016: Chemistry in Combustion Process, 2016.

[32] P. Basu, Biomass Gasification, Pyrolysis and Torrefaction, 2nd ed., Academic Press, 2013, pp. 10, 151.

[33] M. J. Wornat, R. H. Hurt, N. Y. C. Yang and T. J. Headley, "Structural and Compositional Transformations of Biomass Chars during Combustion," *Combustion and Flame,* vol. 100, pp. 131-143, 1995.

[34] F. Mermoud, S. Salvador, L. Van de Steene and F. Golfier, "Influence of the pyrolysis heating rate on the steam gasification rate of large wood char particles," *Fuel,* vol. 85, pp. 1473-1482, 2006.

[35] A. Trubetskaya, P. A. Jensen, A. D. Jensen, M. Steibel, H. Spliethoff and P. Glarborg, "Influence of fast pyrolysis conditions on yield and structural transformation of biomass chars," *Fuel Processing Technology,* vol. 140, pp. 205-214, 2015.

[36] R. Zanzi, K. Sjöström and E. Björnborn, "Rapid high-temperature pyrolysis of biomass in a free-fall reactor," *Fuel,* vol. 75, no. 5, pp. 545-550, 1996.

[37] A. Trubetskaya, G. Surup, A. Shapiro and R. B. Bates, "Modeling the influence of potassium content and heating rateon biomass pyrolysis," *Applied Energy,* vol. 194, pp. 199-211, 2017.

[38] N. M. Laurendeau, "Heterogeneous kinetics of coal char gasification and combustion," *Progress in Energy and Combustion Science,* vol. 4, pp. 221-270, 1978.

[39] M. Gil, J. Riaza, L. Alvarez, C. Pevida, J. Pis and F. Rubiera, "Oxy-fuel combustion kinetics and morphology of coal chars obtained in N2 and CO2 atmospheres in an entrained flow reactor," *Applied Energy,* pp. 67-74, 2012.

[40] M. Gil, J. Riaza, L. Alvarez, C. Pevida and F. Rubiera, "Biomass devolatilization at high temperature under N2 and CO2: Char morphology and reactivity," *Energy,* vol. 91, pp. 655-662, 2015.

[41] A. Trubetskaya, P. A. Jensen, A. D. Jensen, A. D. G. Llamas, K. Umeki and P. Glarborg, "Effect of fast pyrolysis conditions on biomass solid residues at high temperatures," *Fuel Processing Technology,* vol. 143, pp. 118-129, 2016.

[42] M. Zhai, Y. Xu, L. Guo, Y. Zhang, P. Dong and Y. Huang, "Characteristics of pore structure of rice husk char during high-temperature steam gasification," *Fuel,* vol. 185, pp. 622-629, 2016.

[43] R. D. Schultz and A. O. Dekker, "The Absolute Thermal Decomposition Rates Of Solids Part I. The Hot-Plate Pyrolysis of Ammonium Chloride and the Hot-Wire Pyrolysis of Polymethylmethacrylate (Plexiglas IA)," pp. 260-266, 1955.

[44] J. A. Cogliano, "Apparatus for Rapid Pyrolysis Under Controlled Conditions," *AIP Review of Scientific Instruments,* vol. 34, pp. 439-440, 1963.

[45] M. F. Flower, *Combustion of single biomass particles in a heated wire mesh apparatus with video based measurements. (PhD Thesis),* London: Imperial College of Science, Technology & Medicine, University of London, 2010.

[46] R. A. Finch and R. E. Taylor, "Apparatus for Determining Thermophysical Properties of Solids by Direct Electrical Pulse Heating," *AIP Review of Scientific Instruments,* vol. 40, pp. 1195-1199, 1969.

[47] D. B. Anthony, J. B. Howard, H. P. Meissner and H. C. Hottel, "Apparatus for determining high pressure coal-hydrogen reaction kinetics under rapid heating conditions," *AIP Review of Scientific Instruments,* vol. 45, pp. 992-995, 1974.

[48] L. H. Hamilton, A. B. Ayling and M. Shibaoka, "A new experimental device for pyrolysing coal particles under controlled conditions over a wide range of heating rates," *Fuel,* vol. 58, pp. 873-876, 1979.

[49] A.-R. F. Drummond and I. W. Drummond, "Pyrolysis of Sugar Cane Bagasse in a Wire-Mesh Reactor," *Ind. Eng. Chem. Res.,* vol. 35, pp. 1263-1268, 1996.

[50] G. D. Nola, W. d. Jong and H. Spliethoff, "The fate of main gaseous and nitrogen species during fast heating rate devolatilization of coal and secondary fuels using a heated wire mesh reactor," *Fuel Processing Technology,* vol. 90, pp. 388-395, 2009.

[51] M. J. Prins, J. Linden, R. J. M. Bastiaans, J. A. van Oiljen, M. Alden and L. P. H. Goey, "Visualization of Biomass Pyrolysis and Temperature Imaging in a Heated-Grid Reactor," *Energy & Fuels,* vol. 23, pp. 993-1006, 2009.

[52] Y. Zhang, Y. Niu, H. Zou, Y. Lei, J. Zheng, H. Zhuang and S. Hui, "Characteristics of biomass fast pyrolysis in a wire-mesh reactor," *Fuel,* vol. 200, pp. 225-235, 2017.

[53] R. Garcia, C. Pizarro, A. Lavin and J. Bueno, "Biomass proximate analysis using thermogravimetry," *Bioresource Technology,* vol. 139, 2013.

[54] E. Hoekstra, W. P. van Swaaiji, S. R. Kersten and K. J. Hogendoorn, "Fast pyrolysis in a novel wire-mesh reactor: Design and initial results," *Chemical Engineering Journal,* vol. 191, pp. 45-58, 2012.

[55] M. Bellais, *Modelling of the pyrolysis of large wood particles. PhD Thesis.,* Stockholm: KTH - Royal Institute of Technology, 2007.

[56] "Lab&Process," [Online]. Available: https://www.labandprocess.com/en/products/tga-4000. [Accessed July 2018].

[57] S. V. Vassilev, K. Kitano and C. G. Vassileva, "Relations between ash yield and chemical and mineral composition of coals," *Fuel,* vol. 76, pp. 3-8, 1997.

[58] C. J. Hindmarsh, K. M. Thomas, W. X. Wang, H. Y. Cai, A. J. Güell, D. R. Dugwell and R. Kandiyoti, "A comparison of the pyrolysis of coal in wire-mesh entrained-flow reactors," *Fuel,* vol. 74, no. 8, pp. 1185-1190, 1995.

[59] D. Pottmaier, M. Costa, T. Farrow, A. M. Oliveira, O. Alarcon and C. Snape, "Comparison of Rice Husk and Wheat Straw: From Slow and Fast Pyrolysis to Char Combustion," *Energy & Fuels,* vol. 27, pp. 7115-7125, 2013.

[60] M. K. Misra, K. W. Ragland and A. J. Baker, Wood Ash Composition as a Function of Furnace Temperature, vol. 4, USA, Madison: Biomass and Bioenergy, 1993, pp. 103-116.

[61] X. Wu, Z. Zhang, G. Piao, X. He, Y. Chen, N. Kobayashi, S. Mori and Y. Itaya, "Behavior of Mineral Matters in Chinese Coal Ash Melting during char-CO2/H2O Gasification Reaction," *Energy & Fuels,* vol. 23, pp. 2420-2428, 2009.

[62] X. Zhang, H. Zhang and Y. Na, "Transformation of Sodium during the Ashing of Zhundong Coal," *Procedia Engineering,* vol. 102, pp. 305-314, 2015.

[63] S. K. Badholiya and A. Kothari, "A REVIEW ON ASH AGGLOMERATION PHENOMENON IN FLUIDISED BED COMBUSTION BOILER," *International Journal of Scientific Research Engineering & Technology,* vol. 5, no. 11, pp. 533-541, 2016.

[64] R. Swietlik, M. Trojanowska, M. Lozynska and A. Molik, "Impact of solid fuel combustion technology on valence speciation of chromium in fly ash," *Fuel,* vol. 137, pp. 306-312, 2014.

[65] J. M. Johansen, J. G. Jakobsen, F. J. Frandsen and P. Glarborg, "Release of K, Cl, and S during Pyrolysis and Combustion of High-Chlorine Biomass," *Energy & Fuels,* vol. 25, pp. 4961-4971, 2011.

[66] J. N. Knudsen, *Volatilization of Inorganic Matter during Combustion of Annual Biomass. PhD Thesis,* Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2004.

[67] J. S. Chinchon, X. Querol, J. L. Fernandez-Turiel and A. Lopez-Soler, "Environmental Impact of Mineral Transformations Undergone During Coal Combustion," *Environ Geol Water Sci Vol.,* vol. 18, no. 1, pp. 11-15, 1991.

[68] S. Krerkkaiwan, C. Fushimi, A. Tsutsumi and P. Kuchonthara, "Synergetic effect during co-pyrolysis/gasification of biomass and sub-bituminous coal," *Fuel Processing Technology,* vol. 115, pp. 11-18, 2013.

[69] X. Yao, K. Xu, F. Yan and Y. Liang, "Ashing temperature & slaggling," *BioResources,* vol. 12, no. 1, pp. 1593-1610, 2017.

[70] E. Cetin, B. Moghtaderi, R. Gupta and T. F. Wall, "Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars," *Fuel,* vol. 83, pp. 2139-2150, 2004.

[71] Y. Shen, "Chars as carbonaceous adsorbents/catalysts for tar elimination during biomass pyrolysis or gasification," *RenewableandSustainableEnergyReviews,* vol. 43, pp. 281-295, 2015.

[72] J. Fermoso, M. V. Gil, A. G. Borrego, C. Pevida, J. J. Pis and F. Rubiera, "Effect of the Pressure and Temperature of Devolatilization on the Morphology and

Steam Gasification Reactivity of Coal Chars," *Energy & Fuels,* vol. 24, pp. 5586-5595, 2010.

[73] F. Zeng, "Organic and Inorganic Geochemistry of Coal," *Coal, Oil Shale, Natural Bitumen, Heavy Oil and Peat,* vol. 1.

[74] K. L. Manquais, C. Snape, I. McRobbie, J. Barker and V. Pellegrini, "Comparison of the Combustion Reactivity of TGA and Drop Tube Furnace Chars from a Bituminous Coal," *Energy Fuels,* vol. 23, pp. 4269-4277, 2009.

[75] A. Trubetskaya, P. A. Jensen, A. D. Jensen and M. Steibel, "Comparison of high temperature chars of wheat straw and rice husk with respect to chemistry, morphology and reactivity," *Biomass and Bioenergy,* vol. 86, pp. 76-87, 2016.

[76] A. Borrego, L. Garavaglia and W. Kakreuth, "Characteristics of high heating rate biomass chars prepared under N2 and CO2 atmospheres," *International Journal of Coal Geology,* vol. 77, pp. 409-415, 2009.

[77] E. Cetin, R. Gupta and B. Moghtaderi, "Effect of pyrolysis pressure and heating rate on radiata pine char structure and apparent gasification reactivity," *Fuel,* vol. 84, pp. 1328-1334, 2005.

[78] R. Zanzi, K. Sjöström and E. Björnbom, "Rapid pyrolysis of agricultural residues at high temperature," *Biomass and Bioenergy,* vol. 23, pp. 357-366, 2002.

[79] T. S. Farrow, C. Sun and C. E. Snape, "Impact of biomass char on coal char burn-out under air and oxy-fuel conditions," *Fuel,* vol. 114, pp. 128-134, 2013.

[80] K. Jayaraman, I. Gokalp and S. Bostyn, "High ash coal pyrolysis at different heating rates to analyze its char structure, kinetics and evolved species," *Journal of Analytical and Applied Pyrolysis,* vol. 113, pp. 426-433, 2015.

[81] G. Ö. Çakal, H. Yücel and A. G. Gürüz, "Physical and chemical properties of selected Turkish lignites and their pyrolysis and gasification rates determined by thermogravimetric analysis," *Journal of Analytical and Applied Pyrolysis,* vol. 80, pp. 262-268, 2007.

[82] L. Burhenne, M. Damiani and T. Aicher, "Effect of feedstock water content and pyrolysis temperature on the structure and reactivity of spruce wood char produced in fixed bed pyrolysis," *Fuel,* vol. 107, pp. 836-847, 2013.

[83] M. Morin, S. Pecate, E. Masi and M. Hemati, "Kinetic study and modelling of char combustion in TGA in isothermal conditions," *Fuel,* vol. 203, pp. 522-536, 2017.

[84] M. Dall'Ora, P. A. Jensen and A. D. Jensen, "Suspension Combustion of Wood: Influence of Pyrolysis Conditions on Char Yield, Morphology, and Reactivity," *Energy & Fuels,* vol. 22, pp. 2955-2962, 2008.

[85] Z. Zhou, L. Ding, L. Wu, S. Lin, T. Cui, G. Yu and F. Wang, "Comparison of Structure and Gasification Reactivity of Rapid Pyrolysis Chars of Coal Water Slurries and Parent Coals," *Energy Technology,* pp. 284-291, 2014.

[86] A. Bridgwater, Advances in Thermochemical Biomass Conversion, 1 st ed., vol. 1, Switzerland: Springer-Science+Business Media, B.V., 1994, pp. 157-165.

[87] J.-M. Huang and K. E. Daugherty, "Catalytic Effect of Alkali Carbonates on the Calcination of Calcium Carbonates.," *Thermochimica Acta,* vol. 115, pp. 57-62, 1987.