

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**CLASSIFICATION AND EVALUATION OF BIOMASS IN
TURKEY REGARDING TO CONFORMITY ASPECT OF
THERMOCHEMICAL TECHNOLOGIES**

MAHMUT ATEŞ
**A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE**
DEPARTMENT OF CHEMICAL ENGINEERING

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TERMOKİMYASAL TEKNOLOJİLERE
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YÜKSEK LİSANS TEZİ
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SUMMARY

Ten different non-edible biomass feedstocks (orange filter cake, pomegranate filter cake, poplar branch, corn stalk, sugarcane bagasse, olive pomace, hazelnut glume, hazelnut shell, walnut shell and pistachio shell) were chosen to evaluate their potential for thermochemical processes. Biomass feedstocks were characterized by ultimate and proximate analyses. Thermogravimetric analysis (TGA) of biomass feedstock samples was carried out under pyrolysis conditions to compare their thermochemical reactivities. The reactivity to pyrolysis for all biomass feedstock samples was calculated by a model-fitting method, namely Coats-Redfern method. Ultimate analysis showed that poplar branch had the highest hydrogen/carbon atomic ratio ($H/C=1.3$) while hazelnut shell had the lowest H/C ratio of 0.9. Fixed carbon content was the lowest in pistachio shell (16.1%) and the highest in pomegranate filter cake (26.8%). The lowest ash content (1.4%) was found for sugarcane bagasse while the highest ash content (9%) was determined for corn stalk. Hazelnut glume had the highest lignin content (38.9%) while orange filter cake was the lowest lignin content (4.9%). Poplar branch had the lowest char yield at 900 °C (10.8%). Poplar branch and sugarcane bagasse had high degrees of devolatilization. Activation energy (E_a) values for biomass feedstocks changed between 17.8 and 89.3 kJ/mol with $R^2 \geq 0.96$. The lowest E_a (17.8 kJ/mol) was obtained for orange filter cake. Based on all the analyses performed on biomass feedstock samples, orange filter cake, pomegranate filter cake, poplar branch and sugarcane bagasse were found to be the most appropriate biomass feedstocks for thermochemical conversion technologies.

Key Words: Biomass, Energy, Waste, Pyrolysis, Char yield, Thermochemical.

ÖZET

Yenilebilir olmayan 10 biyokütle örneği (portakal filtre keki, nar filtre keki, kavak dalı, mısır sapı, şeker kamışı posası, zeytin prinası, fındık kavuzu, fındık kabuğu, ceviz kabuğu ve fıstık kabuğu) termokimyasal işlemler bakımından uygunluklarının değerlendirilmesi amacıyla seçilmiştir. Biyokütle örneklerinin karakterizasyonu elementel ve kısa analiz yöntemleriyle yapılmıştır. Biyokütle örneklerinin termogravimetrik analizleri (TGA) termokimyasal reaktivitelerini karşılaştırmak amacıyla piroliz koşullarında gerçekleştirilmiştir. Çalışılan biyokütle örneklerinin piroliz koşullarındaki reaktiviteleri bir model yakınsama yöntemi olan Coats-Redfern metodu ile hesaplanmıştır. Elementel analiz sonuçlarına göre kavak dalı en yüksek hidrojen/karbon atomik oranına ($H/C=1.3$), fındık kabuğu en düşük H/C (0.9) oranına sahip biyokütle olmuştur. Sabit karbon içeriği en az olan fıstık kabuğu (%16.1) olurken en yüksek sabit karbon içeriği nar filtre keki (%26.8) olmuştur. Kül içeriği en az olan şeker kamışı posası (%1.4) iken en yüksek kül içeriği mısır sapında (%9) belirlenmiştir. Fındık kavuzu en yüksek lignin içeriğine (%38.9) sahip olurken portakal filtre keki en düşük lignin içeriğine (%4.9) sahip olan örnek olmuştur. Kavak dalı 900 °C sıcaklıkta en düşük yakma verimine (%10.8) sahip biyokütle olmuştur. Kavak dalı ve şeker kamışı posasının en yüksek ağırlık kaybı hızına sahip biyokütller olduğu belirlenmiştir. Biyokütle örneklerinin aktivasyon enerjisi (E_a) değerleri 17.8 ile 89.3 kJ/mol arasında değişmiş ve $R^2 \geq 0.96$ olarak bulunmuştur. Portakal filtre keki en düşük E_a (17.8 kJ/mol) değerine sahip biyokütle örneği olmuştur. Gerçekleştirilen analizlerin sonucunda; portakal filtre keki, nar filtre keki, kavak dalı ve şeker kamışı posası termokimyasal dönüşüm teknolojilerine en uygun biyokütller olarak belirlenmiştir.

Anahtar Kelimeler: Biyokütle, Enerji, Atık, Piroliz, Yakma verimi, Termokimyasal.

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LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations</u> <u>and Acronyms</u>	<u>Explanations</u>
A	: Arrhenius constant
E _a	: Activation energy
m ³	: Cubic meter
°C	: Degree Celcius
mg	: Milligram
kg	: Kilogram
min	: Minute
ml	: Milliliter
wt. %	: Weight percent
%	: Percent
μm	: Micrometer
P	: Pressure
R ²	: Pearson coefficient of determination
T	: Temperature
mm	: Millimeter
s	: Second
rpm	: Revolution per minute
Mtoe	: Million tons of oil equivalent
J	: Joule
kJ	: Kilo Joule
EJ	: Exa Joule
kcal	: Kilocalorie
R	: Ideal gas constant
α	: Degree of conversion
DTG	: Differential thermogravimetry
IEA	: International Energy Agency
OECD	: Organization for Economic Co-Operation and Development
TGA	: Thermal Gravimetric Analysis

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1. INTRODUCTION

Biomass feedstocks are converted to solid, liquid and gas products by thermal decomposition processes. These products can be used in electricity generation and industrial applications. Sunflower shell was processed to obtain liquid products and parameters affecting biomass liquefaction efficiency was analyzed [Özyurt, 2006]. Pinecone, soybean pomace, corn stalk and peanut shell were analyzed to determine their pyrolysis performance, and among them pinecone showed the best pyrolysis performance [Varol, 2007]. Sour cherry seed and sour cherry seed shells were used as waste lignocellulosic biomasses, and their thermal conversions were analyzed by pyrolyzing them in two different reactors under nitrogen atmosphere [Duman, 2009]. Thermal decomposition behavior of olive cake, hazelnut shell, sugarcane bagasse and corn cob were investigated under nitrogen atmosphere at different heating rates and kinetic parameters were calculated [Çelebi, 2011]. Pyrolysis was used to determine pyrolysis kinetics of pinenut cone, olive pomace and sunflower shell by using thermogravimetric analysis method [Mutlu, 2012]. Apricot kernel was pyrolyzed, and effect of temperature, reaction time and sweeping gas flow rate on liquid, solid and gas yields were studied [Tunçok, 2013]. Effects of temperature and catalyst on pyrolysis of wheat straw, barley straw, oat straw and corn cob were investigated [Işıkdag, 2007]. Sawdust is an important biomass source used for the production of bioenergy and liquid biofuels by pyrolysis. Fast pyrolysis of pinecone sawdust was carried out to determine effects of various factors including temperature, reaction time, pyrolysis temperature, nitrogen flow rate and particle size on pyrolysis product diversity. Liquid products obtained were analyzed by using spectroscopic and chromatographic methods [Kanmaz, 2011].

Various biomass feedstocks have been utilized for pyrolysis primarily to obtain energy from these renewable energy sources. Although some studies with regard to the investigation of thermal decomposition and thermochemical conversion of agricultural based biomasses as waste materials exist in literature, studies considering the use of agricultural non-edible biomass feedstocks for thermochemical processes are scarce. Therefore, determination of suitable biomass feedstocks for pyrolysis can be achieved by comparing pyrolysis behavior and reactivity of biomass feedstocks.

1.1. Hypothesis

The hypothesis of this study is that thermochemical conversion of agricultural based biomass feedstocks can be studied by using thermogravimetric analysis techniques, and suitability of these biomass feedstocks for thermochemical processes can be determined by comparing pyrolysis behavior and reactivity of biomass feedstocks.

1.2. Objectives

The objectives of this study are to:

- i) conduct proximate analysis and ultimate analysis for the selected agricultural based biomass feedstocks, and compare biomass feedstocks' performances
- ii) analyze thermogravimetric analysis results of all biomass feedstocks
- iii) perform kinetic analysis by using Coats-Redfern method
- iv) estimate char yields of all biomass feedstocks
- v) determine appropriate biomass feedstocks for thermochemical applications.

2. BIOMASS

The entire processing track of biomass (Figure 2.1) [Werpy and Peterson, 2004] as renewable energy source is depending on the type of biomass and its physical characteristics and chemical composition. In the past few decades, comprehensive studies of the physical characteristics and chemical composition of biomass fuels have been carried out, and these are still being continued to obtain more insight into the reactive behavior of these fuels under different processing conditions [Huber and Dumesic, 2006].

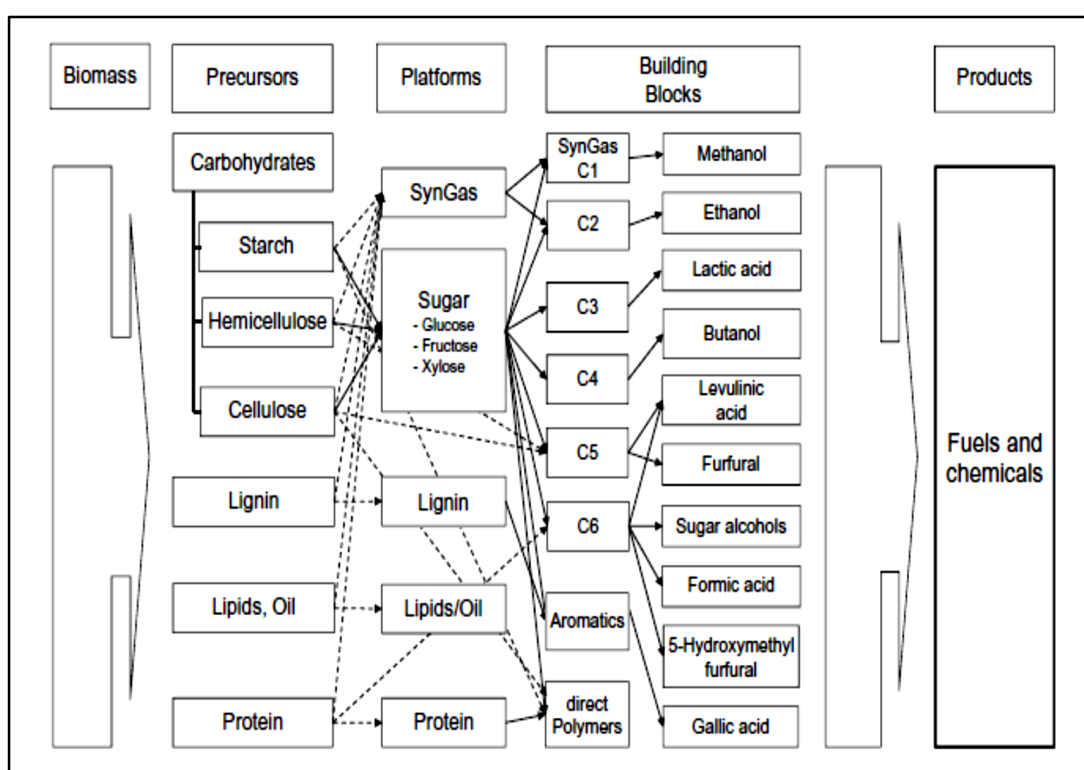


Figure 2.1: Bio-based product flowchart for biomass feedstocks.

2.1. Common Compounds in Lignocellulosic Biomass Feedstocks

Lignocellulosic biomass (Figure 2.2) is composed of three main macromolecules: cellulose (40-60 wt%), hemicellulose (10-30 wt%) and lignin (20-25 wt%) which are organized in a complex network in the plant cell wall [Zakzeski et al., 2010].

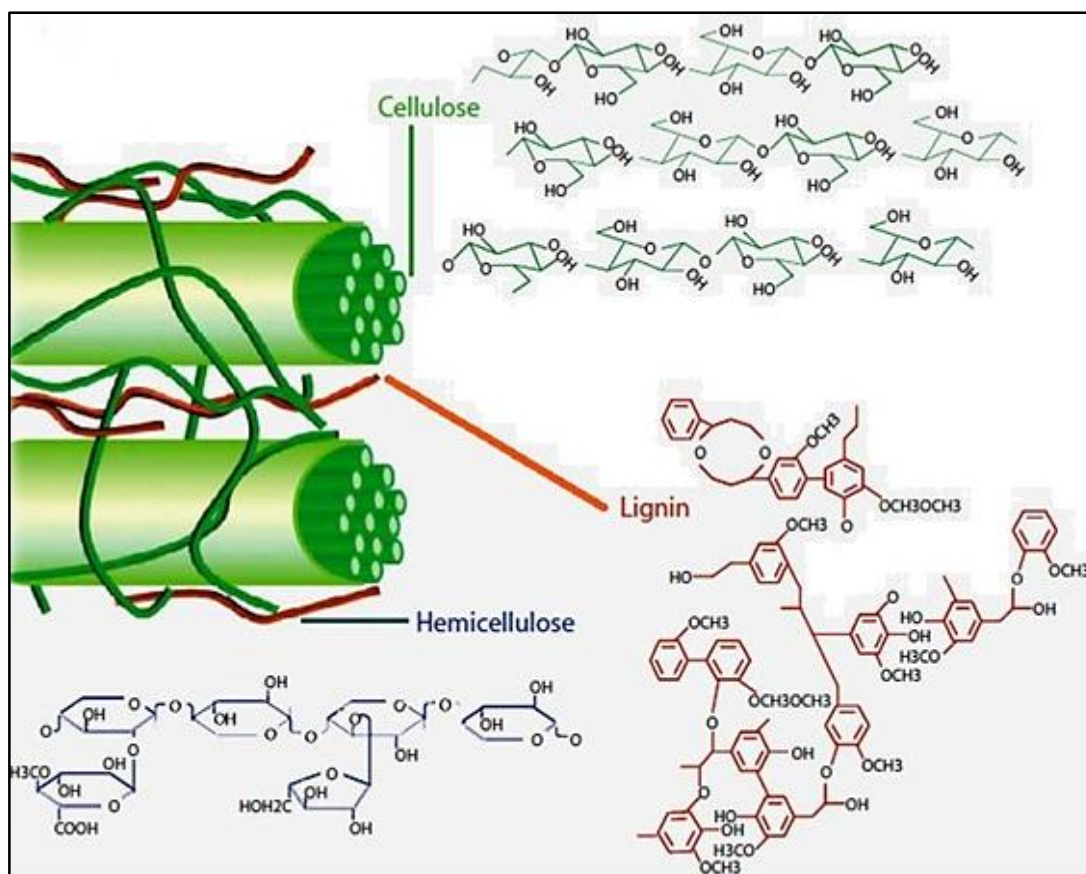


Figure 2.2: Structure of lignocellulosic biomass.

2.1.1. Cellulose

Cellulose (Figure 2.2) [Alonso et al., 2012] is a homopolysaccharide $(C_6H_{10}O_5)_n$ of glucose C_6 sugar (hexosan) units that constitutes the main part of the cell walls of plants and synthesized in photosynthesis reaction [Kamm et al., 2006]. During the biosynthesis of cellulose, the cellulose molecules pile onto each other forming microfibrils which form both crystalline and amorphous regions. The microfibrils aggregate into fibrils with diameters of 30–100 nm and lengths of 100–500 nm. Finally, these fibrils aggregate into cellulose fibers with diameters of 100–400 nm and lengths of 0.5–4 mm [Klemm et al., 1998]. Cellulose forms the raw material for many manufactured goods such as paper, paperboard, rayon and cellophane [Simon et al., 1998]. Cellulose structure shows that $-OH$ groups form both inter- and intramolecular hydrogen bonds, which cause different polymer chains to arrange themselves in parallel configurations to form a crystalline supermolecular structure. This structure ensures a relatively high stability against thermal and biochemical degradations

compared to hemicellulose and starch. This resulting structure makes cellulose completely insoluble in ordinary aqueous solutions. The linear cellulose chains form bundles that tend to twist so as to make ribbon like microfibrilic anisotropic (highly ordered) structures that are highly oriented in the cell wall structure [Balat et al., 2009].

2.1.2. Hemicellulose

Hemicelluloses (Figure 2.2) are known to occur in several structural varieties in terrestrial plants and algae and, even in different plant tissues, within one plant. They are composed of both linear and branched heteropolymers of D-xylose, L-arabinose, D-mannose, D-glucose, D-galactose, L-rhamnose, L-fucose and D-glucuronic acid, which may be acetylated or methylated. In contrast to cellulose, which is a homopolymer, hemicelluloses represent a type of heterogeneous polysaccharides. They are short, highly branched polymers of six-carbon (C_6) sugars like glucose, mannose, galactose and five-carbon (C_5) sugars as xylose and arabinose and glucose derivatives such as glucuronic acid [Amidon et al., 2011]. Important aspects of the structure and composition of hemicelluloses are the lack of crystalline structure and the presence of acetyl groups in the polymer chain [Harmsen et al., 2010]. Therefore, hemicelluloses are more susceptible to hydrolysis than cellulose [Trajano and Wyman, 2013]. In hardwoods and herbaceous crops, xylans are the prevalent group of hemicelluloses [Spiridon and Popa, 2008]. Hemicellulose extracted from plants possess a high degree of polydispersity, polydiversity and polymolecularity. However, degree of polymerization of hemicellulose does not usually exceed 300 units whereas the minimum limit can be around 50 monomers [Ragauskas, 2014].

2.1.3. Lignin

Lignin (Figure 2.2) is an amorphous polymer consisting of a complex and heterogeneous three-dimensional network of aromatic substructures that provides coherence and toughness and, together with cellulose, forms the woody cell walls of plants and the cementing material between them. Most biomass consists of 20–30 wt% lignin, which is deposited between the spaces of the cells, a growth-related process called lignification [De Jong, 2015]. Lignin is primarily aromatic in nature. Its basic molecular units are linked mostly by ether bonds, but carbon-to-carbon linkages exist

as well. Different functional side groups can be distinguished such as hydroxyl, methoxyl and carbonyl groups. Covalent bonds exist with both hemicelluloses and cellulose rendering improved mechanical strength to the plant [Jacobsen and Wyman, 2000]. Lignin is produced in large quantities as by-product of the pulp and paper industry, which needs cellulose fibers with a low lignin content, and it mostly serves as heat supply fuel. It can also be used as the substrate for the production of high-value-added products such as vanillin, phenol and derived phenolic resins. Lignin also plays a role in rubber production and antioxidant generation [Pye, 2006]. Lignin has intrinsic biodegradability and it is believed that the incorporated polymers within lignin would be more biodegradable than the petroleum based polymers [Xu and Ferdosian, 2017].

2.2. Biomass Energy in the World

Biomass is scientifically defined as any organic matter derived from plants or animals available on a renewable basis. Biomass includes wood and agricultural crops, herbaceous and woody energy crops, municipal organic wastes as well as manure [IEA, 2012]. Biomass has been continuing to increase its popularity especially against energy crisis situations for decades. In 2017, the share of renewable energy sources (Figure 2.3) in total OECD primary energy supply reached about 10.2% [IEA, 2018].

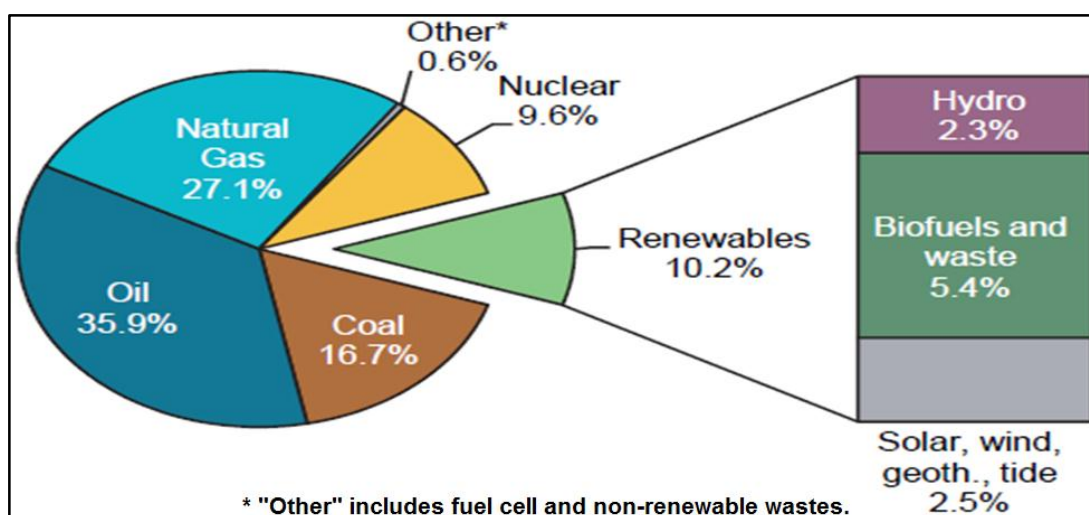


Figure 2.3: World total primary energy supply in 2017.

In OECD countries, total primary energy supply from renewable sources increased from 272 Mtoe to 539 Mtoe between 1990 and 2017, an average annual growth of 2.6%. Bio-based renewable energy sources (Figure 2.4) which consist of liquid biofuels, municipal wastes, solid biofuels and biogases have the biggest contribution (53.5%) in terms of sustainability and renewability to meet primary energy demand in OECD countries in 2017 [IEA, 2018].

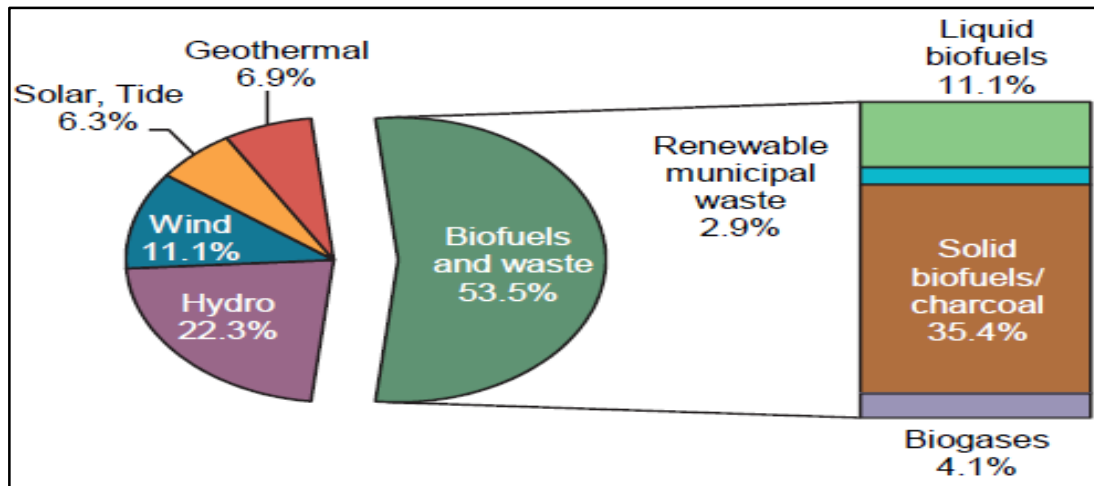


Figure 2.4: Renewable energy supply for OECD countries in 2017.

2.3. Biomass Energy in Turkey

Turkey has a strong growing population with migrations, births, economic and technological developments [OECD, 2018]. Because of these reasons, primary energy demand of Turkey (Figure 2.5) is increasing from 100 Mtoe to 160 Mtoe in the last decade [BP Statistical Review, 2018].

Turkey's primary energy supply is basically consisted of oil, natural gas and coal [BP Statistical Review, 2018]. Turkey has not sufficient hydrocarbon resources, so it is highly dependent on imported primary energy sources to meet the needs of country. Almost all oil (93%) and natural gas (99%) demands are supplied by import [Furuncu and Özdemir, 2018]. Furthermore, amount of coal imported was about 54% of all coal demand in 2017 [TKİ, 2017]. In the light of the foregoing energy data, renewables are crucial energy matters which have potential to supply energy security for Turkey [Hache, 2018].

National oil and lignite reserves are not sufficient to soothe country energy deficit. Due to the increasing energy demand of households and industries, environmental pollution may become a serious problem in the future for the country. In this scope, renewable energy issues seem to be one of the cost efficient and technically effective solutions for sustainable energy development frame and environmental pollution prevention in Turkey [Ocak et al., 2004]. Biomass primarily must be supported and seriously couraged by governments for households and private sectors. Biomass-based conventional fuels predominate in rural areas energy demands; almost all the biomass energy is consumed for the heating and cooking needs of rural people [Kaygusuz and Bilgen, 2008], [Kaygusuz, 2009].

Biomass feedstocks are used to meet a variety of energy needs including heating homes, fueling vehicles and providing process heat for industrial facilities. Biomass potential includes wood, animal and plant wastes [Saracoglu, 2010]. In Turkey, biomass energy is used in the form of noncommercial fuel depending on the classical one. There is a considerable potential to expand use of biomass by dealing large volumes of unused residues and wastes. Based on this various range of feedstocks, the technical potential for biomass is about 1300 EJ/year by 2030 although most biomass supply scenarios that take into account sustainability constraints indicate an annual feasible potential of between 200 and 500 EJ [Kotcioğlu, 2011].

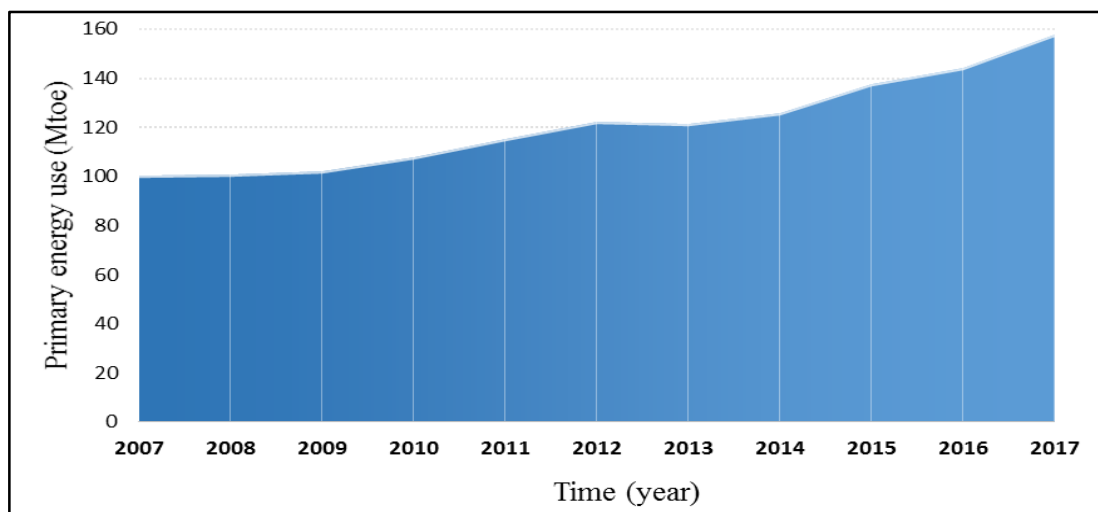


Figure 2.5: Annual change of primary energy use of Turkey.

Main biomass potential of Turkey is based on wheat straw, woody materials, cocoon shell, hazelnut shell, grain dust, crop residues and fruit tree residues

[Melikoglu, 2013]. Among the biomass energy sources, fuel wood seems to be the most interesting because its share in the total energy production of Turkey is high (14%). The total biomass energy potential of Turkey is reported around 33 Mtoe [Toklu, 2017].

2.3.1. Agricultural Based Biomass in Turkey

Wood, crop and animal wastes from classical biomass sources have been used especially in heating and cooking purposes in Turkey for many years. By using agricultural biomass feedstocks, most European countries are reducing both energy imports and increasing rural development. According to the data (Table 2.1), Turkey has roughly 16 Mtoe agricultural and plant waste-based energy potential [Yörük and Özen, 2014].

Table 2.1: Biomass potential of Turkey in terms of biomass sources.

Source	Potential (Mtoe)	Share (%)
Animal waste based energy	1.32	11
Agricultural and plant waste based energy	15.94	78
Municipality waste based energy	2.19	7
Forest waste based energy	0.86	4
Total	20.31	

It is reported that fruit tree pruning is a valuable matter for renewable energy [Bilandzija et al., 2012], [Dyjakon et al., 2016]. Amount of tree pruning (kg per tree) can be estimated to change from 0.9 kg to 9.1 kg for various type of fruit trees (apple, peach, apricot, plum and walnut). Turkey has a huge biomass feedstock potential to supply for fruit tree-based biomass energy (Table 2.2) [TUIK-1, 2018]. Pruning is a process which aims to decrease number of young branching by cutting young branches to focus on main branches to achieve higher harvest yield. After the pruning process, considerable amount of tree branches will be available for alternative use in biomass energy sector. Hazelnut, olive and apple trees are the highest potential for biomass feedstocks in Turkey. Amount of fruit trees pruning based biomass feedstock is estimated as 0.5-5 million tons.

Table 2.2: Annual numbers of important fruit and nut trees for Turkey (millions).

Year	Apple	Apricot	Olive	Orange	Peach	Plum	Pomegranate	Hazelnut	Walnut
2013	63	17	167	15	16	10	16	356	11
2014	66	17	169	15	16	10	18	355	12
2015	71	18	172	15	17	10	17	366	13
2016	73	18	174	15	18	11	17	368	15
2017	75	19	175	14	18	10	17	370	17

Residue per product ratio is the key term for evaluation of agricultural-based biomass feedstocks. It is dependent on a number of factors (crop yield, crop area, type of crop, etc.). Average amount of crop-based biomass feedstock [TUIK-2, 2018] is estimated as 12-72 million tons (Table 2.3) using residue per product ratio values reported by Daioglou et al. 2016 [Daioglou et al., 2016].

Table 2.3: Annual production of important agricultural crops for Turkey (thousand tons).

Year	Wheat	Barley	Corn	Sunflower	Seed cotton	Sugar beet
2013	22,050	7,900	5,900	1,523	2,250	16,489
2014	19,000	6,300	5,950	1,638	2,350	16,743
2015	22,600	8,000	6,400	1,681	2,050	16,023
2016	20,600	6,700	6,400	1,671	2,100	19,593
2017	21,500	7,100	5,900	1,964	2,450	21,149

2.3.2. Forest Based Biomass in Turkey

Turkey's forestland has an area of approximately 22.3 million hectares and covers 28.6% of the surface area of the entire country. In the last decade, wood production capacity of Turkish forests was between 13-17 million m³. Pruning, maintenance and inspection works are carried out at specific time intervals in the forests. Forest fires and landslides damage to the forests, and a considerable waste solid biomass, named forest waste, emerges. Forest trees pruning and other forest arrangement facilities residues create annually about 5-10 million m³ biomass from Turkish forests [Yıldırım, 2015].

2.4. Thermochemical Technologies

Thermochemical processes aim at converting biomass into heat, electricity and liquid or gaseous biofuels. Biomass feedstocks are also spontaneously vulnerable to decomposition by time and atmospheric conditions. Therefore, these energy vectors are more convenient to be valorized than the solid biomass [van Swaaij et al., 2015]. From left to right (Figure 2.6), the processes are ranked as a function of the extent of oxidation of biomass: combustion (excess of air) to gasification (lower amount of air brought in the process) to liquefaction (reduction, no air) [Dufour, 2016].

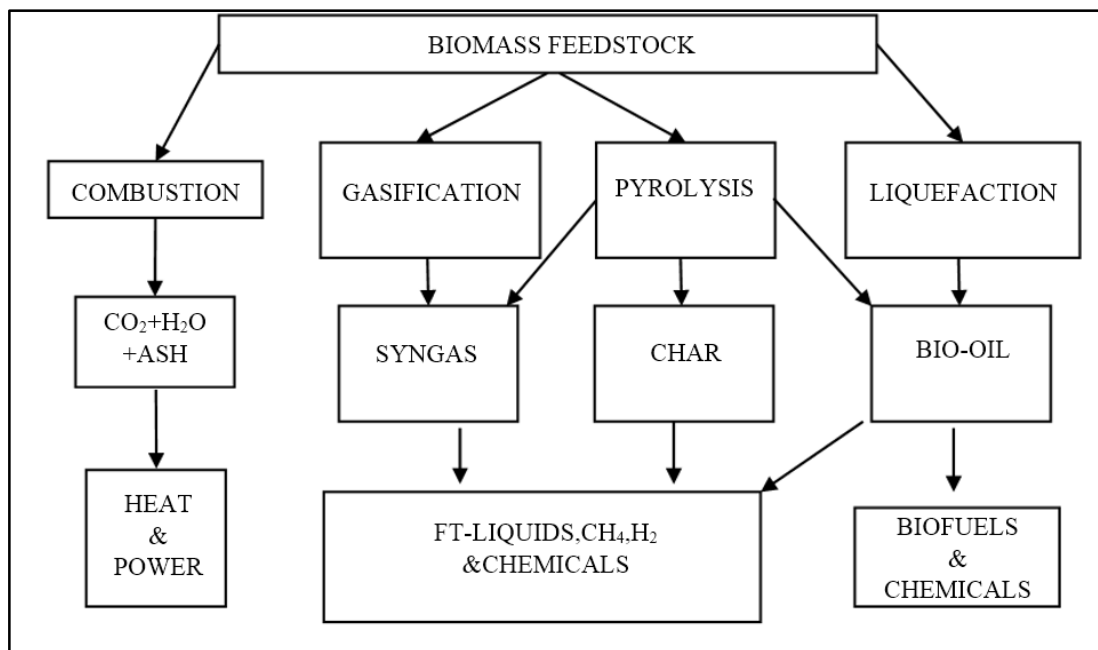


Figure 2.6: Overview of main thermochemical processes for biomass.

2.4.1. Combustion of Biomass

Combustion is the well-known technology for biomass utilization, especially for generating heat and steam from woody fuels. A biomass feedstock combustion facility can generate steam energy, electricity energy or both [Beck, 2003]. Biomass combustion is a complex process that consists of consecutive heterogeneous and homogeneous reactions. The main processing steps are drying, devolatilization, gasification, char combustion and gas-phase oxidation. The time used for each reaction

depends on the fuel size and properties, temperature and combustion conditions [Sadaka and Johnson, 2017].

2.4.2. Pyrolysis of Biomass

Pyrolysis is thermal degradation of organic material in the absence of (molecular) oxygen. It is a versatile thermal conversion technology that comes into several varieties depending on the desired products. Main pyrolysis methods and their major products are given in Table 2.4 [Bridgwater, 2015].

Hemicellulose, cellulose and lignin are all organic parts of lignocellulosic biomass, but their thermochemical behaviors are noticeably different due to their physical and chemical properties [Yang et al., 2006].

Table 2.4: Pyrolysis methods and major products.

Method	Retention time	Heating rate	Temperature (K)	Products
Carbonization	days	very low	673	solid
Pressurized	15 min-2 hours	medium	723	solid
Traditional	5-30 min	low	873	oil, gas, liquid
Fast pyrolysis	0.5-5 seconds	very high	923	fuel oil
Flash-liquid	< 1second	high	< 923	fuel oil
Flash-gas pyrolysis	< 1second	high	< 923	chemical, gas
Ultra-pyrolysis	< 0.5 second	very high	1,273	chemical, gas
Vacuum pyrolysis	2-30 seconds	medium	673	fuel oil
Hydro-pyrolysis	< 10 seconds	high	< 773	fuel oil
Methano-pyrolysis	< 10 seconds	high	> 973	chemical

The rate of thermal breakdown and the product slate are determined by the order of thermochemical stability of the individual biomass constituents that range from hemicellulose (fast degassing/decomposition from 200–300 °C) as the least stable polymer to the more stable cellulose (fast degassing/decomposition from 300–400 °C) (Figure 2.7) [Wild, 2011]. Lignin exhibits intermediate thermal degradation behavior (gradual degassing/decomposition from 250–500 °C) [Koukios, 1993].

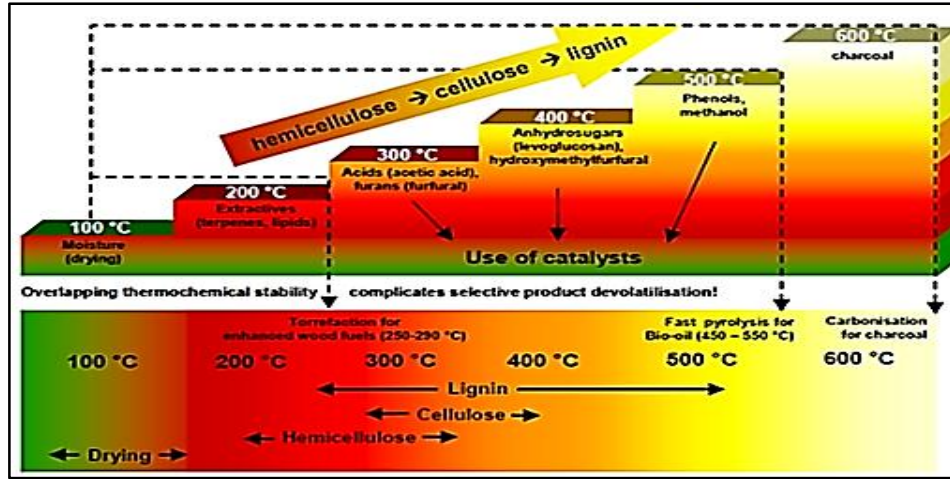


Figure 2.7: Pyrolysis processes for lignocellulosic materials.

2.4.3. Gasification of Biomass

Gasification is thermochemical conversion of an organic material into a valuable gaseous product, called syngas, and a solid product, called char. The biomass gasification represents an efficient process for the production of power and heat, and the production of hydrogen and second-generation biofuels [Molino et al., 2016].

Gasification operations are simultaneous reactions. Fundamental gasification reactions constitute [Maschio et al., 1994], [Higman and van der Burgt, 2008]:

Combustion reactions:



Boudouard reaction:



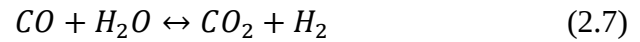
Water gas shift reaction:



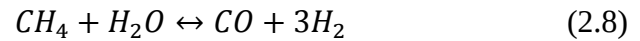
Methanation reaction:



CO shift reaction:



Steam methane reforming reaction:



Gasifier design depends basically on the reactor hydrodynamics. The hydrodynamic parameters (bed velocity, feeding amount, pressure difference and temperature difference) determine the interaction between biomass and gasifying agent [E4tech and NNFCC, 2010]. There are various gasifier types. Well-known types [Ptasinski et al., 2009] are fixed bed, fluidized bed and entrained flow gasifiers (Figure 2.8).

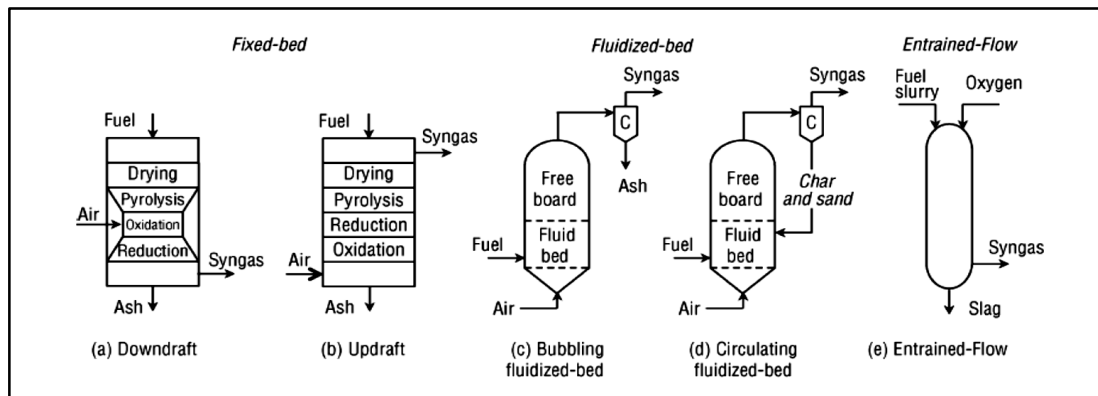


Figure 2.8: Well-known gasifier types.

3. EXPERIMENTAL

3.1. Materials

Biomass samples (Table 3.1) were supplied from various geographic locations in Turkey. Until they were used in the experiments, the samples were kept under dark conditions in glass jars placed in a cold room at 4 ± 0.5 °C (Figure 3.1).

Table 3.1: Biomass feedstock samples.

Sample Name	Geographical location
Orange filter cake	Adana
Pomegranate filter cake	Adana
Poplar branch	Samsun
Corn stalk and leaves	Adana
Sugarcane bagasse	Konya
Olive pomace	Balıkesir
Hazelnut glume	Giresun
Hazelnut shell	Giresun
Walnut shell	Tokat
Pistachio shell	Gaziantep



Figure 3.1: Biomass feedstock samples.

3.2. Preparation of Samples for Analysis

Biomass feedstocks (1000 g for each sample) were finely ground in a grinder (Jaw Crusher BB 200, Retsch GmbH, Germany) operating at 1500 rpm for 15 min. After grinding, biomass feedstocks were dried at 105 °C in an oven (Binder VDL115, Binder GmbH, Germany) until the constant weight was attained to facilitate sample preparation and minimize biological activity. Dried biomass feedstocks were classified using a wire-mesh sieve (250 µm, Retsch GmbH, Germany) to ensure the homogeneity of the samples. Undersize fraction was used in analyses and experiments.

3.3. Methods

3.3.1. Ultimate Analysis of Biomass Samples

Carbon, hydrogen and nitrogen content analyses were carried out according to ASTM D5373-14 [ASTM D5373-14, 2014]. Sulfur and oxygen contents of the biomass feedstocks were done in accordance with ASTM D4239-14 and ASTM D3176-15, respectively [ASTM D4239-14, 2014], [ASTM D3176-15, 2015].

3.3.2. Proximate Analysis of Biomass Samples

Moisture content, ash, volatile substances and fixed carbon, and calorific values were determined according to ASTM D7582-15, ASTM E1755-01, ASTM D3175-17 and ASTM D5865-13, respectively [ASTM D7582-15, 2015], [ASTM E1755-01, 2015], [ASTM D3175-17, 2017], [ASTM D5865-13, 2013].

3.3.3. Lignin Analysis

Lignin contents of biomass samples were analyzed according to ASTM D1106-96 [ASTM D1106-96, 2013].

3.3.4. Thermogravimetric Analysis

Thermogravimetric analyses of biomass feedstock samples were carried out by using a dynamic mixed gas sorption analyzer (IGA-003, Hiden Isochema, Kochel, Germany) at a heating rate of 20 °C/min. A sample mass of 10 ± 0.5 mg was used, and measurements were carried out in duplicate. TGA program was started purging with nitrogen for 15 min to remove adsorbed impurities on the surface layer of the samples. After purging, first heating program was started from 20 °C to 120 °C under nitrogen with a flow rate of 60 ml/min. First holding step was started when the temperature was reached to 120 °C. Constant temperature condition was kept at 120 °C for 50 min under nitrogen atmosphere. After drying, second heating step was started from 120 °C to 900 °C under nitrogen with a flow rate of 60 ml/min. Second holding step was started when temperature was reached to 900 °C. Constant temperature condition was kept at 900 °C for 50 min under nitrogen atmosphere.

Char yield is based on residue which contains both carbon and ash [Qu et al., 2011] as given below:

$$\text{Char yield \%} = \frac{m_y}{m_0} \times 100 \quad (3.1)$$

where m_0 and m_y refer to initial and final masses at reference temperature (600 and 900 °C), respectively.

3.3.5. Analysis of Decomposition Behavior by Coats-Redfern Method

Upon being subjected the biomass feedstocks to thermal treatment, decomposition reaction of a biomass (X) in a solid phase takes place according to the Eq. (3.2):



The thermal decomposition data of the biomass feedstock samples obtained with TGA was processed by using integral methods to determine decomposition kinetics of

the biomass feedstocks. The Coats-Redfern method was used to investigate the thermal decomposition kinetics of biomass feedstocks.

Coats-Redfern method is derived from Arrhenius equation and used to estimate the pre-exponential factor and the apparent reaction order. The equations for the Coats-Redfern method are given by the following equations [Coats and Redfern, 1964].

The degree of conversion in pyrolysis reaction can be obtained by the following equation:

$$\alpha = \frac{m_0 - m_i}{m_0 - m_f} \quad (3.3)$$

where m_0 , m_i and m_f refer to initial, instantaneous and final masses, respectively, and α is the degree of conversion.

The general non-isothermal decomposition reaction rate is expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3.4)$$

where $f(\alpha)$ represents reaction model and $k(T)$ is the rate constant as expressed by the Arrhenius equation given below;

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (3.5)$$

where A is the pre-exponential factor, E_a is the activation energy of the reaction, R is the universal gas constant and T is the absolute temperature. By substituting Eq. (3.5) into Eq. (3.4) gives:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (3.6)$$

Taking into account that the temperature is a function of time and it is increasing with a constant heating rate (β), the following expressions are derived:

$$T = \beta t + T_0 \quad (3.7)$$

$$dT = \beta dt \quad (3.8)$$

$$f(\alpha) = (1 - \alpha)^n \quad (3.9)$$

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (3.10)$$

where n is the reaction order. By substituting Eq. (3.5) into Eq. (3.10) and integrating it, the following expression can be obtained [Bedoui et al., 2016]:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E_a}{RT}\right) dT \quad (3.11)$$

The integration of Eq. (3.11) has no exact solution. That's why, the exponential expression within this integration has to be defined as an asymptotic series. The integration of this series expansion while ignoring higher order terms gives:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{\beta E_a} \left[1 - \frac{2RT}{E_a}\right] \exp\left(\frac{-E_a}{RT}\right) \quad (3.12)$$

Using natural logarithm of Eq. (3.12) and taking $n=1$, the equation simplifies to;

$$\ln \left[\frac{\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right) \right] - \frac{E_a}{RT} \quad (3.13)$$

E_a was calculated from the plot of $\ln \left[\frac{\ln(1-\alpha)}{T^2} \right]$ versus $\frac{1}{T}$.

Assuming the term $\frac{2RT}{E_a} \ll 1$, Eq. (3.12) reduces to:

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[\frac{AR}{\beta E_a} \right] - \frac{E_a}{RT} \quad (3.14)$$

In this case, E_a was calculated from the plot of $\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right]$ versus $\frac{1}{T}$.

4. RESULTS and DISCUSSION

4.1. Characterization, and Ultimate and Proximate Analyses

Ultimate analysis of hazelnut glume, hazelnut shell, walnut shell, poplar branch and pistachio shell showed low oxygen/carbon atomic ratios of 0.61, 0.66, 0.71, 0.82 and 0.83, respectively, compared to corn stalk (O/C=1.01), pomegranate filter cake (O/C=0.96), sugarcane bagasse (O/C=0.91), olive pomace (O/C=0.91) and orange filter cake (O/C=0.90) (Table 4.1). The highest hydrogen/carbon atomic ratio was obtained for the poplar branch (H/C=1.3) while the lowest hydrogen/carbon atomic ratio was determined for the hazelnut shell (H/C=0.9) (Table 4.1). Among ten biomass feedstock samples, the lowest sulfur content was found for the hazelnut shell (0.05%) while the hazelnut glume (0.15%) had the highest sulfur content. Nitrogen content of the hazelnut glume was the highest (1.25%), but the nitrogen content of the corn stalk was the lowest (0.13%) among ten biomass feedstock samples.

Table 4.1: Ultimate analysis of biomass feedstock samples.

Sample	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	O/C	H/C
			(wt%-dry basis)				
Orange filter cake	48.57	6.31	1.13	0.11	43.88	0.90	1.2
Pomegranate filter cake	47.90	5.50	0.67	0.10	45.84	0.96	1.2
Poplar branch	51.23	6.35	0.49	0.13	41.81	0.82	1.3
Corn stalk	47.24	4.76	0.13	0.12	47.75	1.01	1.0
Sugarcane bagasse	48.89	5.66	0.70	0.10	44.65	0.91	1.2
Olive pomace	48.96	5.55	0.68	0.11	44.70	0.91	1.2
Hazelnut glume	57.77	5.75	1.25	0.15	35.07	0.61	1.0
Hazelnut shell	56.74	5.07	0.46	0.05	37.69	0.66	0.9
Walnut shell	54.84	5.50	0.44	0.12	39.10	0.71	1.0
Pistachio shell	50.88	6.03	0.41	0.10	42.58	0.83	1.2

A comparison of the proximate analysis results, calorific values and lignin contents of the biomass feedstocks is given in Table 4.2. Since the reactivity of volatile gases is much higher than the solid portion, the quantity of volatile matter is a distinctive property for the choice and dimensioning of thermochemical systems. Pistachio shell had the highest volatile matter (82.1%) while hazelnut glume had the lowest volatile matter (60.7%). The volatile matter of other biomass feedstocks changed between 69.3%-78.3%. Fixed carbon was the lowest in the pistachio shell samples (16.1%), but it was the highest in the pomegranate filter cake samples (26.8%). Ash content in biomass feedstocks causes agglomeration and slag deposit which are resulted in air pollution emission, vessel corrosion and utilization problems [Koppejan and Brem, 2008]. The lowest ash (1.4%) was found for the sugarcane bagasse while the highest ash content (9%) was determined for the corn stalk.

Biomass feedstock samples used in this study, except orange filter cake had calorific values above 4000 kcal/kg. The highest calorific value (4900 kcal/kg) was obtained for the hazelnut shell (Table 4.2).

Table 4.2: Characteristics, proximate analysis, calorific value and lignin contents of biomass feedstock samples.

Sample	Moisture content of original sample (wt%-wet basis)	Volatile matter	Fixed carbon	Ash content	Calorific value (kcal/kg)	Lignin content (wt%-dry basis)
Orange filter cake	84.5	75.2	21.1	3.7	3,985	4.9
Pomegranate filter cake	73.6	69.3	26.8	3.9	4,044	9.7
Poplar branch	13.9	78.3	17.6	4.1	4,656	34.0
Corn stalk	6.7	72.9	18.1	9.0	4,503	28.0
Sugarcane bagasse	6.7	78.1	20.5	1.4	4,368	29.0
Olive pomace	19.3	74.6	19.4	6.0	4,851	36.0
Hazelnut glume	47.8	60.7	23.5	8.9	4,372	38.9
Hazelnut shell	5.7	72.5	25.6	1.9	4,900	35.8
Walnut shell	8.5	74.2	23.8	1.9	4,625	30.5
Pistachio shell	4.7	82.1	16.1	1.9	4,561	32.7

Lignin contents of biomass feedstock samples varied between 4.9% and 38.9% (Table 4.2). Hazelnut glume had the highest lignin content (38.9%) while orange filter cake was the lowest lignin content (4.9%). 35.1% lignin was found for the hazelnut glume [Ceylan and Topçu, 2014], 20-43% lignin was reported for the olive pomace [Kocabaş-Ataklı et al., 2015] and 29.3% lignin was determined for the poplar branch [Adıgüzel, 2013]. The results of lignin analysis conducted in this study are compatible with those reported in literature for the similar biomass feedstocks.

4.2. Thermogravimetric Behavior

Thermogravimetric analysis is the most commonly used tool to obtain experimental kinetic data and predict thermochemical behavior of materials. According to the curves obtained for the TGA analysis, the mass loss range can be divided into three stages. In the first stage, drying (evaporation of moisture) took place between 20 °C and 120 °C. In the second stage, a sharp weight loss peak was observed between ~250 °C and ~550 °C. This sharp peak had a shoulder depending on the sample indicating the presence of hemicellulose and cellulose structures together. In the third stage, from ~550 °C up to ~900°C, the rate of the weight loss decreased markedly and was designated for extended lignin decomposition. Upon shifting from pyrolysis to oxidation atmosphere at 900 °C by changing the flow gas from nitrogen to oxygen, a deep but short weight loss region was observed indicating that the oxidation of the char residue (Figures 4.1 through 4.10). After an additional operation (oxidation step), ash was determined as the inorganic residue upon completion of this oxidation step.

Differential thermogravimetry (DTG) curves showing the change in weight loss with respect to temperature for the biomass feedstock samples are given in Figure 4.11. DTG profile of pomegranate filter cake was different from the DTG profiles of the other biomass feedstock samples. A peak around 250 °C and a shoulder at 350 °C were observed for the pomegranate filter cake. The highest devolatilization rate was obtained for the poplar branch and sugarcane bagasse (Figure 4.11).

Char yield is important to determine suitability of materials including biomass feedstocks for combustion. Sugarcane bagasse had the highest char yield at 600 °C (38.0%) while orange filter cake yielded the lowest char yield at 600 °C (19.8%). Olive pomace had the highest char yield at 900 °C (20.2%) while poplar branch had the

lowest char yield at 900 °C (10.8%). It was determined that the char yield of the walnut shell was about 30% at 650 °C [Uzun and Yaman, 2015] which is comparable with the char yield of the walnut shell (25.7% at 600 °C) obtained in this study. Komnitsas et al. determined that the char yield of the pistachio shell was 14% at 800 °C [Komnitsas et al., 2015] while the char yields obtained for the pistachio shells were 22.0% and 17.5% at 600 °C and 900 °C, respectively. It was reported that the char yield of the corn stalk was 27.4% at 550 °C [Tora et al., 2016] comparable with the char yield of the corn stalk (29.1% at 600 °C) found in the present study.

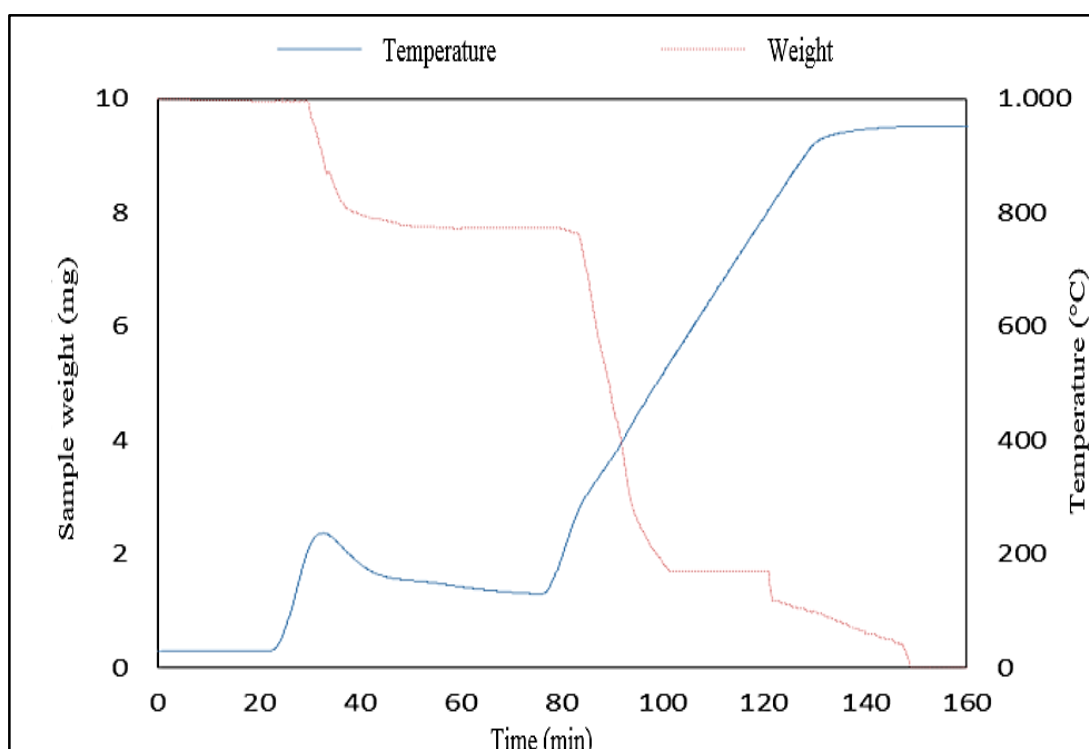


Figure 4.1: Thermogram of orange filter cake at a heating rate of 20 °C/min.

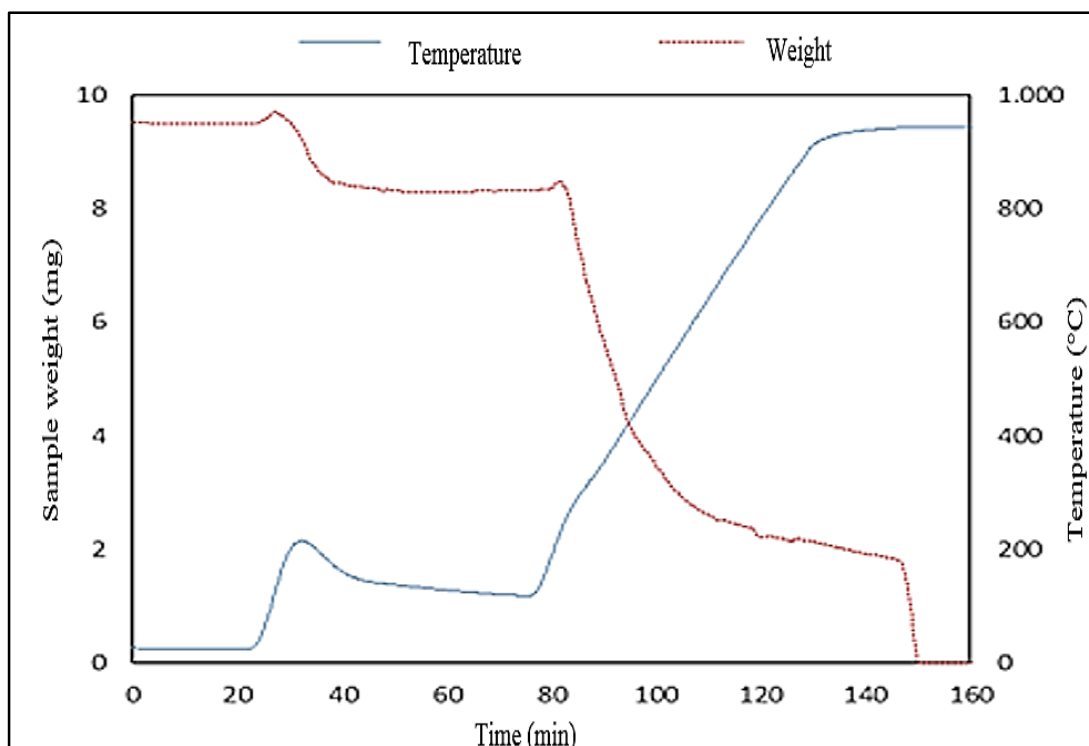


Figure 4.2: Thermogram of pomegranate filter cake at a heating rate of 20 °C/min.

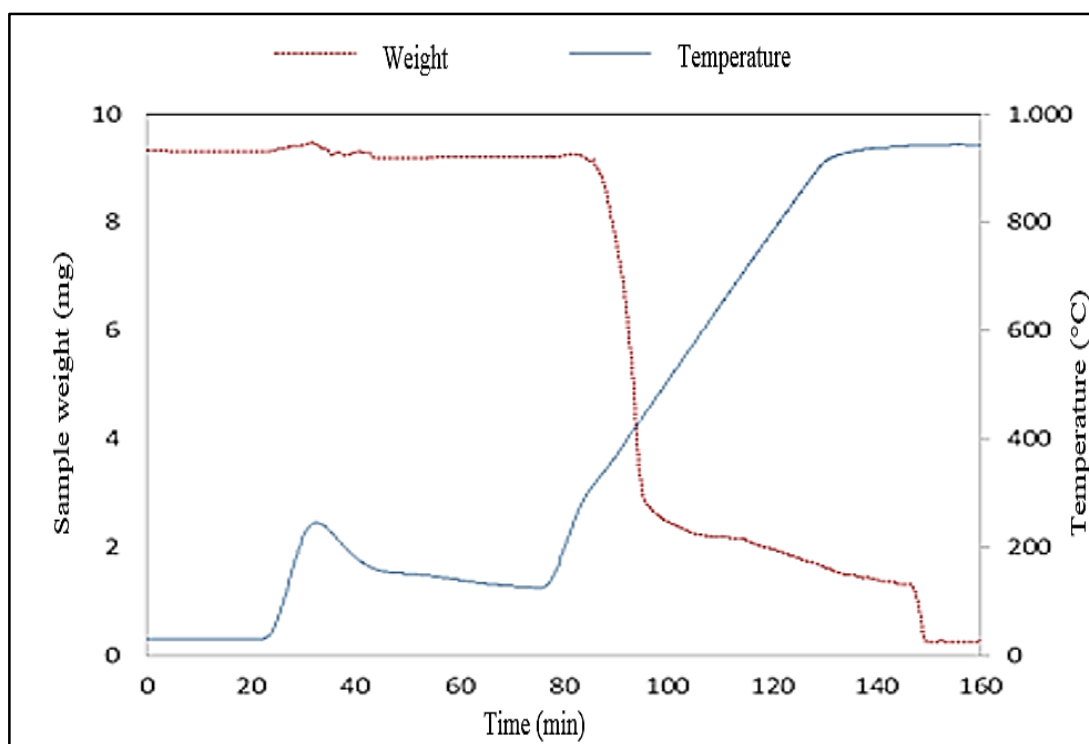


Figure 4.3: Thermogram of poplar branch at a heating rate of 20 °C/min.

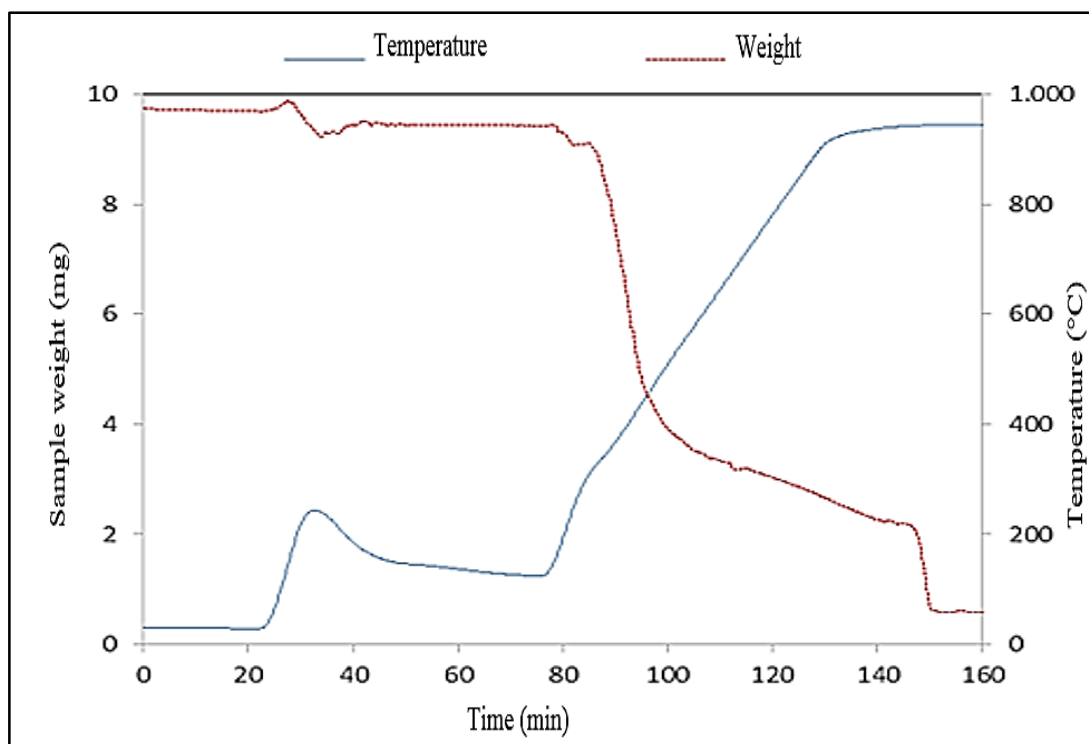


Figure 4.4: Thermogram of corn stalk at a heating rate of 20 °C/min.

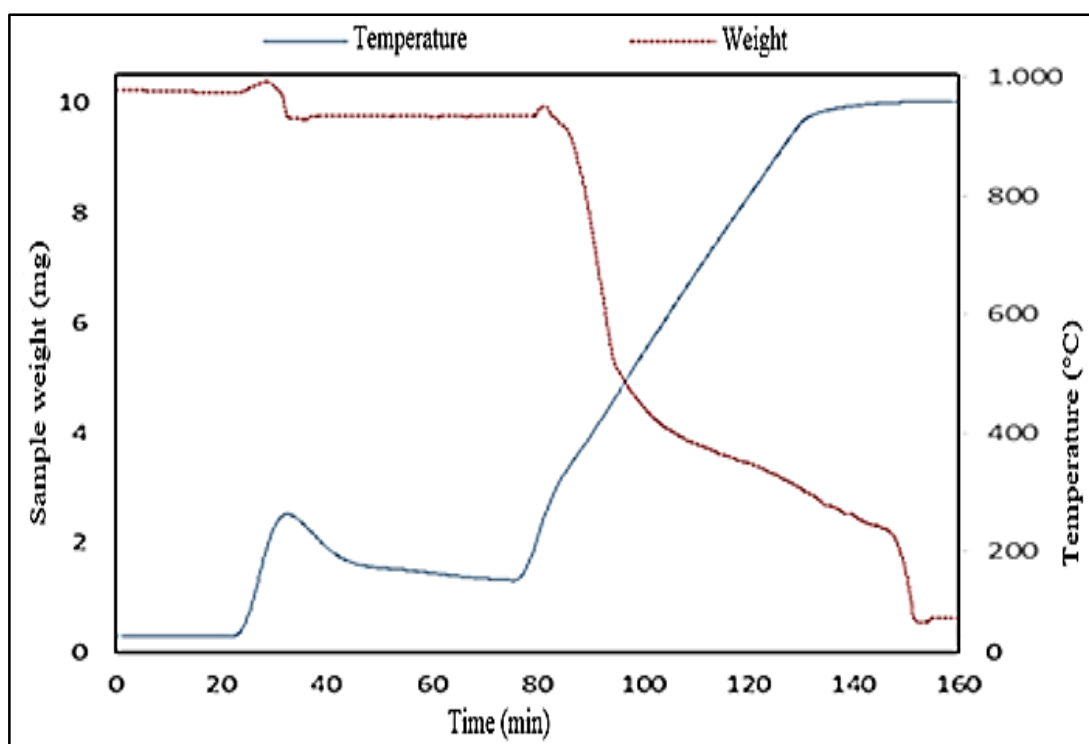


Figure 4.5: Thermogram of sugarcane bagasse at a heating rate of 20 °C/min.

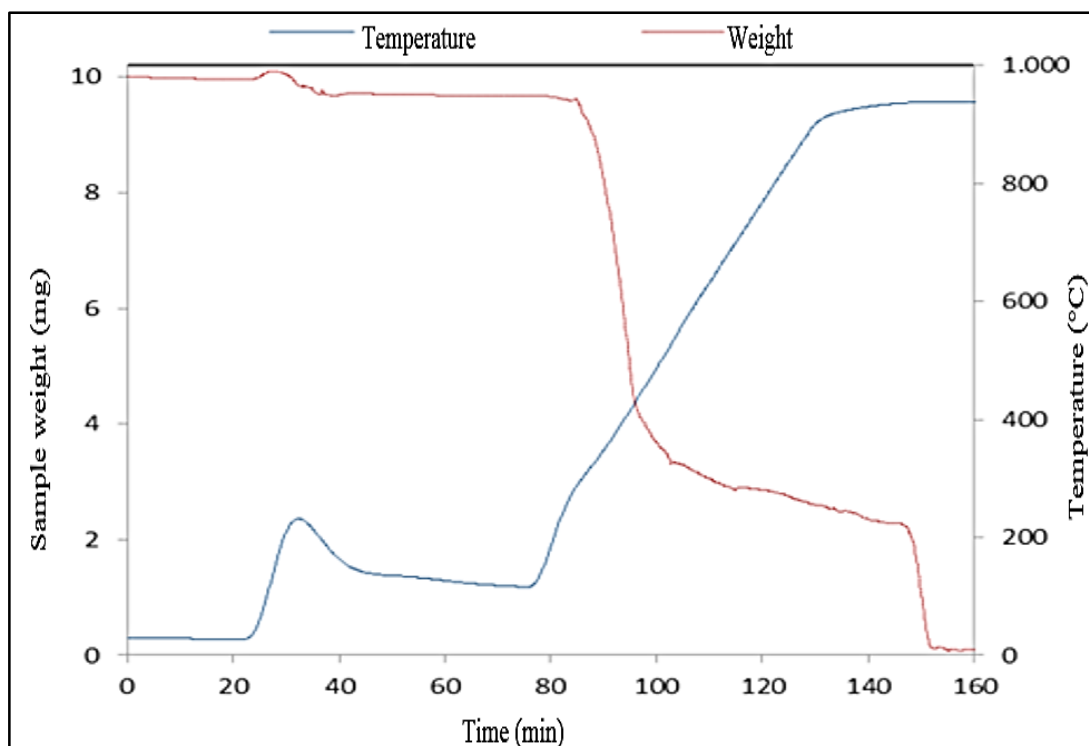


Figure 4.6: Thermogram of olive pomace at a heating rate of 20 °C/min.

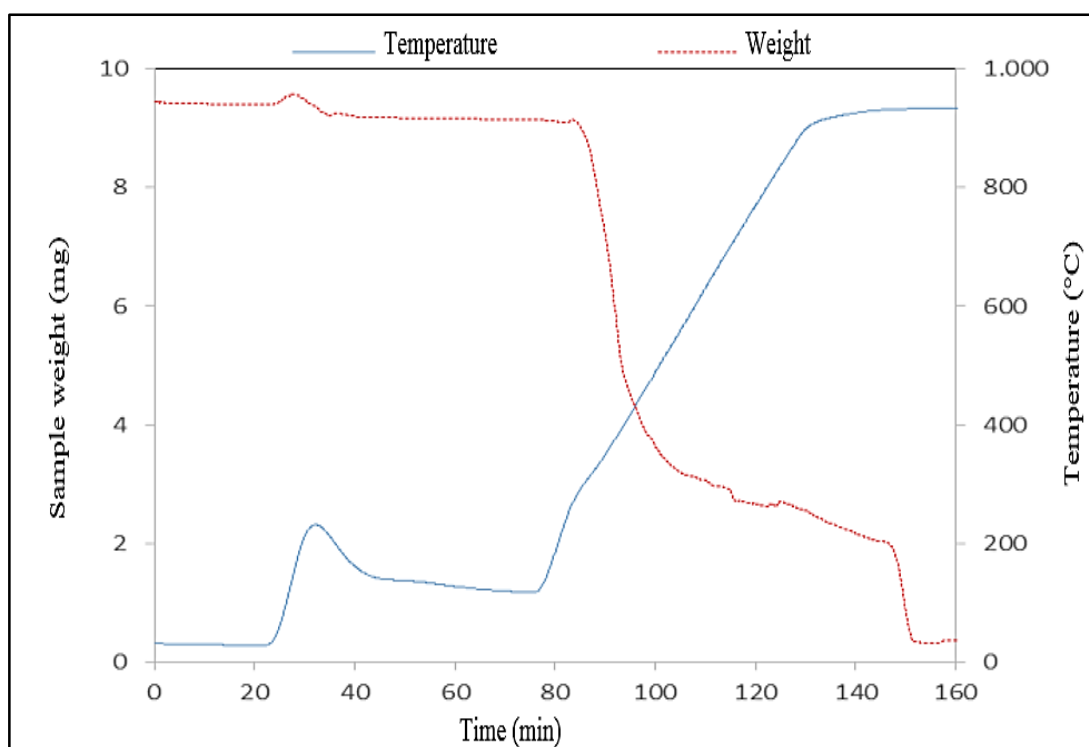


Figure 4.7: Thermogram of hazelnut glume at a heating rate of 20 °C/min.

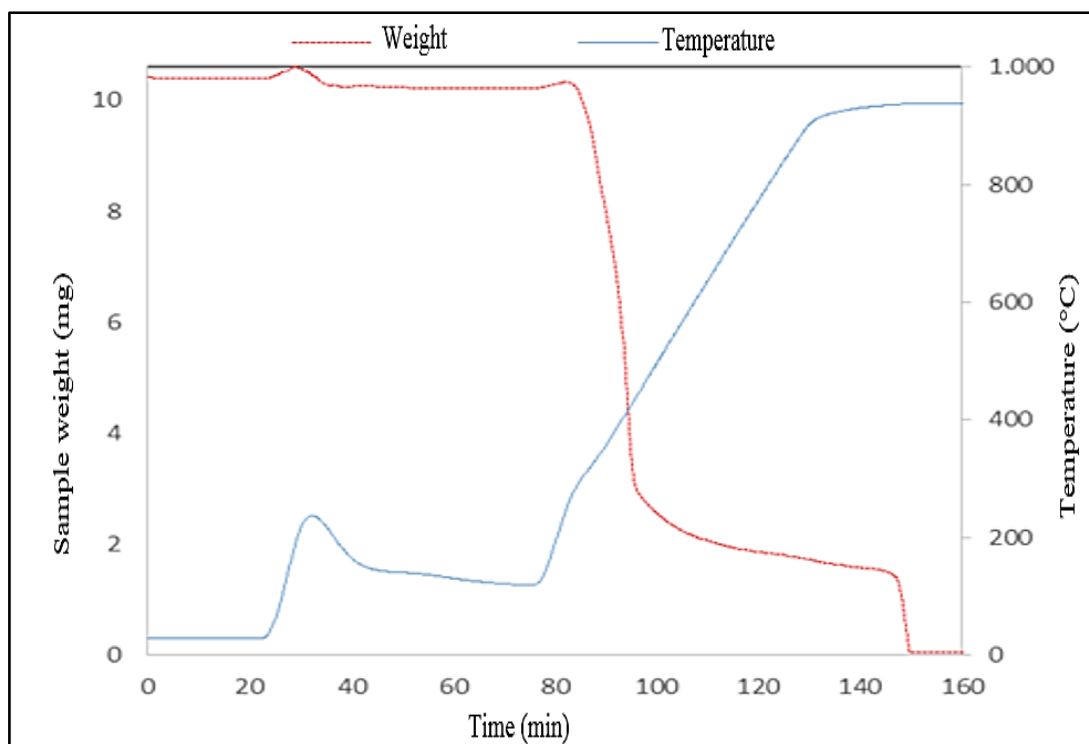


Figure 4.8: Thermogram of hazelnut shell at a heating rate of 20 °C/min.

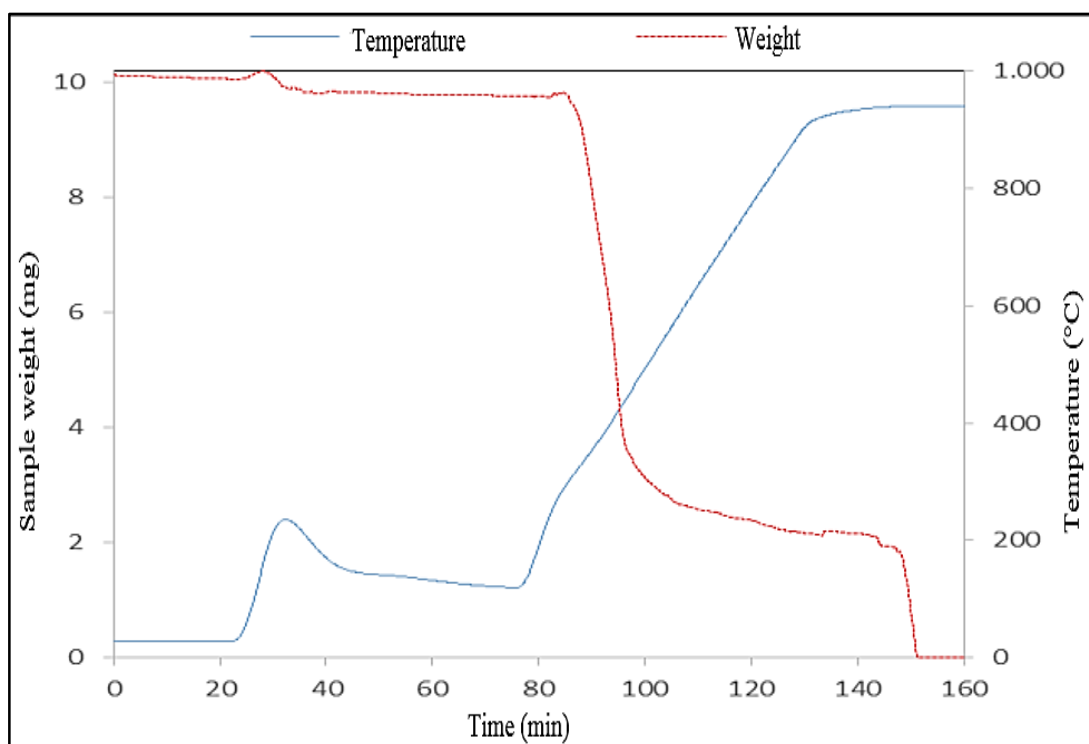


Figure 4.9: Thermogram of walnut shell at a heating rate of 20 °C/min.

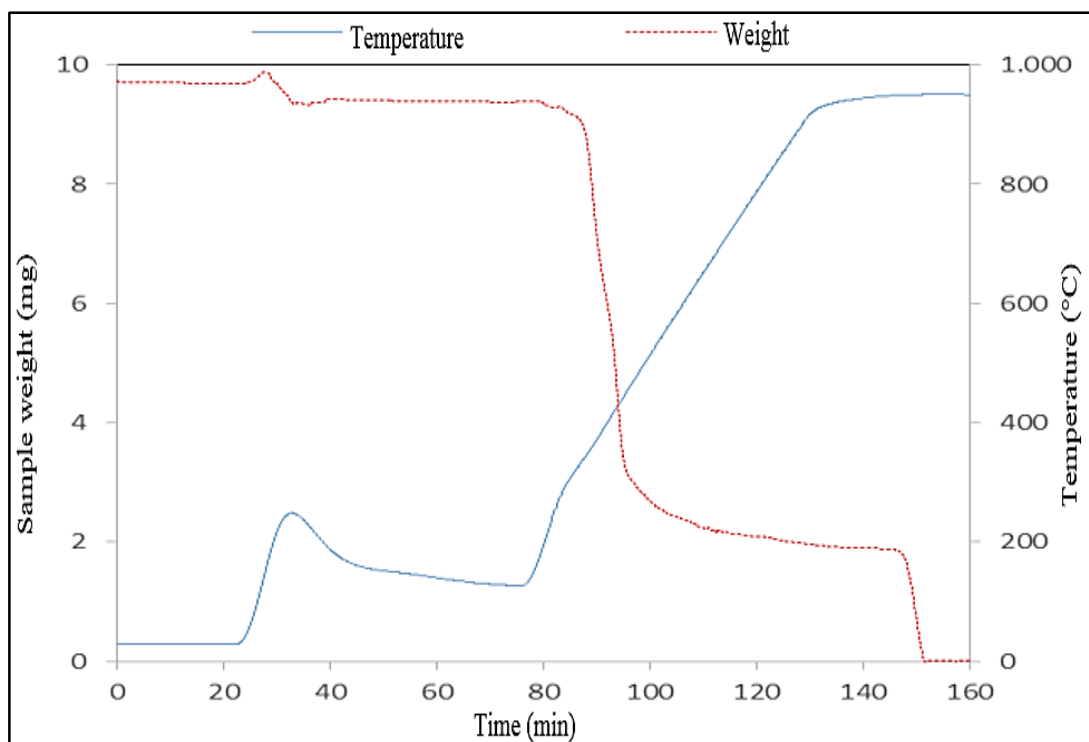


Figure 4.10: Thermogram of pistachio shell at a heating rate of 20 °C/min.

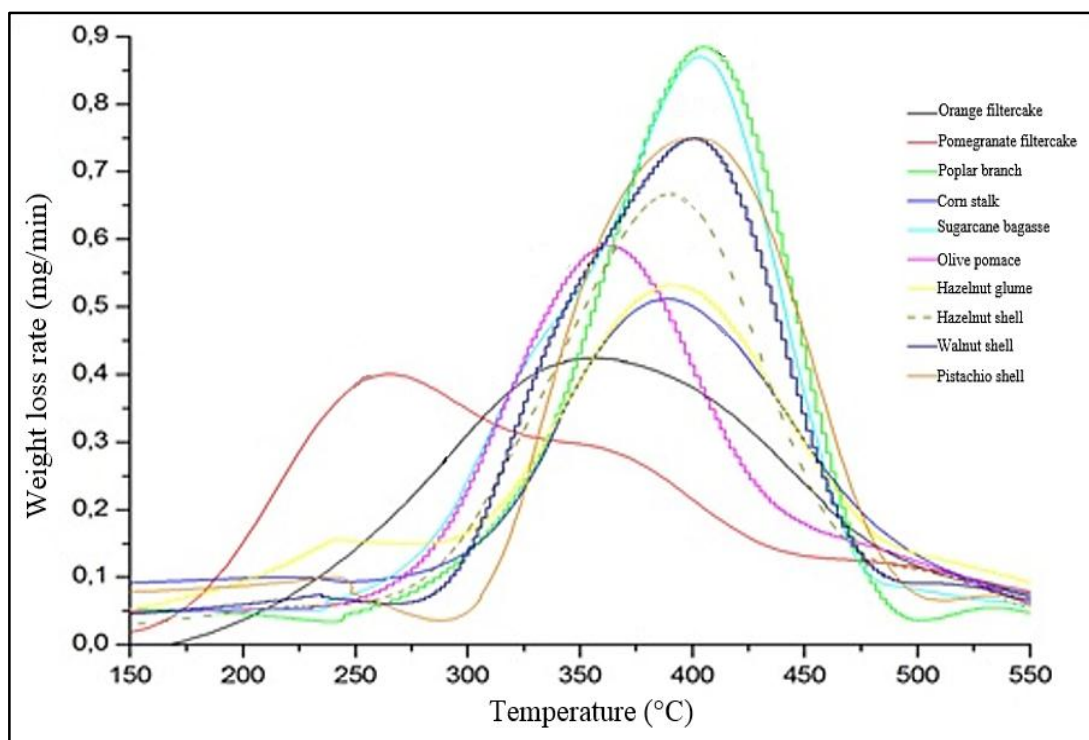


Figure 4.11: Weight loss rate versus temperature data for biomass feedstocks.

Table 4.3: Char yields of biomass feedstock samples.

Sample	Char yield at 600 °C (%)	Char yield at 900 °C (%)
Orange filter cake	19.8	16.6
Pomegranate filter cake	23.2	14.3
Poplar branch	23.7	10.8
Corn stalk	29.1	19.3
Sugarcane bagasse	38.0	11.5
Olive pomace	35.1	20.2
Hazelnut glume	31.3	18.5
Hazelnut shell	21.8	20.1
Walnut shell	25.7	17.8
Pistachio shell	22.0	17.5

The char yield of the olive pomace at 600 °C was found to be 35.1% which is in good agreement with the char yield (32%) reported for the olive pomace at 630 °C by Bedoui et al. (2016) [Bedoui et al., 2016].

4.3. Kinetic Analysis using Coats-Redfern Method

Kinetic parameters for the biomass feedstock samples were calculated for the holocellulose decomposition region, and activation energies together with pre-exponential factors are given in Table 4.4. E_a values for the biomass feedstock samples changed between 17.8 and 89.3 kJ/mol with $R^2 \geq 0.96$. The highest E_a (89.3 kJ/mol) was found for the poplar branch while the lowest E_a (17.8 kJ/mol) was obtained for the orange filter cake. Since activation energy is the minimum energy required to start a reaction, higher E_a values mean slower reactions (Table 4.4).

The E_a value of pomegranate peels determined by Arrhenius equation was reported as 12.72 kJ/mol by Doymaz (2011) [Doymaz, 2011]. In the present study, the E_a value of the poplar branch was obtained as 89.3 kJ/mol which is comparable with the E_a value (79.4 kJ/mol) of the poplar branch determined using Coats-Redfern method as reported by Bay (2006) [Bay, 2006]. The E_a value of the corn stalk obtained

using Ozawa method was 76.7 kJ/mol [Poudel and Oh, 2014]. Mohomane et al. reported E_a value of sugarcane bagasse (151 kJ/mol) using Kissinger method [Mohomane et al., 2017]. Bedoui et al. found E_a values of 85 and 140 kJ/mol for the olive stone using Kissinger-Akahira-Sunose method and Ozawa-Flynn-Wall method, respectively [Bedoui et al., 2016]. Özveren and Özdoğan stated E_a values of 78.7 and 79.9 kJ/mol using Ozawa-Flynn-Wall method and Friedman method, respectively [Özveren and Özdoğan, 2013].

Table 4.4: Kinetic parameters for biomass feedstock samples.

Sample no and name	E_a (kJ/mol)	A	R^2
Orange filter cake	17.8	1.82×10^9	0.97
Pomegranate filter cake	22.5	2.37×10^9	0.96
Poplar branch	89.3	3.75×10^4	0.99
Corn stalk	60.1	2.45×10^6	0.99
Sugarcane bagasse	66.0	1.27×10^6	0.98
Olive pomace	72.6	2.96×10^5	0.99
Hazelnut glume	59.8	4.77×10^6	0.99
Hazelnut shell	60.9	3.20×10^6	0.99
Walnut shell	69.6	7.84×10^5	0.98
Pistachio shell	73.5	4.88×10^5	0.97

In the present study, E_a value of 72.6 kJ/mol was found for the olive pomace using Coats-Redfern method. This result is in close agreement with that of Özveren and Özdoğan [Özveren and Özdoğan, 2013] reported for the olive stone. Ceylan and Topçu determined E_a values for the hazelnut husk as 85 and 140 kJ/mol using Kissinger-Akahira-Sunose and Ozawa-Flynn-Wall methods, respectively [Ceylan and Topçu, 2014]. E_a values between 208-220 kJ/mol were reported for hazelnut shell using Ozawa-Flynn-Wall method by Kocabaş-Ataklı et al. (2015) [Kocabaş-Ataklı et al., 2015] while E_a values between 20-153 kJ/mol were given by Sheth and Babu (2008) [Sheth and Babu, 2008] using differential evolution algorithm method. In the present study, the E_a value of the hazelnut shell (60.9 kJ/mol) determined using Coats-Redfern method is in the range of E_a values reported by Sheth and Babu (2008) [Sheth and Babu, 2008] for the hazelnut shell. Huang et al. determined E_a values of walnut

shell (17.3-56 kJ/mol) using Coats-Redfern method [Huang et al., 2012] which is comparable with the E_a value of the walnut shell (69.9 kJ/mol) determined using Coats-Redfern method in this study. The E_a values of pistachio shells were found to be 122-156 kJ/mol using Coats-Redfern method, 153-187 kJ/mol using Ozawa-Flynn-Wall method and 186-353 kJ/mol using Horowitz-Metzger method [Açıklın, 2012]. The discrepancies in the E_a values in previous studies given in the literature are attributed to the different methods used in the calculation of E_a values.

5. CONCLUSIONS

In this study, thermochemical conversions of ten biomass feedstock samples were studied using thermogravimetric analysis to determine their pyrolysis behaviors. Ultimate analysis, proximate analysis and kinetic calculations using Coats-Redfern method were conducted. Ultimate analysis showed that poplar branch had the highest H/C of 1.3 while hazelnut shell had the lowest H/C of 0.9. Proximate analysis revealed that pistachio shell had the highest volatile matter (82.1%) while hazelnut glume had the lowest volatile matter (60.7%). Fixed carbon content was the lowest in pistachio shell (16.1%) and the highest in pomegranate filter cake (26.8%). The lowest ash content (1.4%) was found for sugarcane bagasse while the highest ash content (9%) was determined for corn stalk. Biomass feedstock samples used in this study, except orange filter cake, had calorific values above 4000 kcal/kg. Lignin contents of biomass feedstock samples varied between 4.9% and 38.9%. Hazelnut glume had the highest lignin content (38.9%) while orange filter cake was the lowest lignin content (4.9%). Sugarcane bagasse had the highest char yield at 600 °C (38.0%) while orange filter cake yielded the lowest char yield at 600 °C (19.8%). Poplar branch and sugarcane bagasse had high degrees of devolatilization. Poplar branch and sugarcane bagasse also showed less charring tendency in which char yields were 10.8% and 11.5% at 900 °C, respectively, meaning that in case of fast pyrolysis where low char and high oil is favored, these two biomass feedstocks would be better options among the other biomass feedstocks studied. Kinetic analysis using Coats-Redfern method revealed that the lowest E_a (17.8 kJ/mol) was obtained for orange filter cake in which lower E_a means higher activity. Based on all the analyses performed on biomass feedstock samples, orange filter cake, pomegranate filter cake, poplar branch and sugarcane bagasse were found to be the most appropriate biomass feedstocks for thermochemical conversion technologies.

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