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INVESTIGATION OF THE NON-ISOTHERMAL COMBUSTION KINETICS OF SOME AGRICULTURAL RESIDUES

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BAZI TARIMSAL ATIKLARIN İZOTERMAL OLMAYAN DURUMDA YANMA KİNETİKLERİNİN İNCELENMESİ

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FOREWORD

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ABBREVIATIONS

MSW	: Municipal Solid Waste
PAH	: Poly-Aromatic Hydrocarbons
IEA	: International Energy Agency
IGAC	: International Global Atmospheric Chemistry
BIBEX	: Biomass Burning Experiment
SRWC	: Short Rotation Woody Crop
FBR	: Fluidized Bed Reactor
NCV	: Net Calorific Value
GCV	: Gross Calorific Value
COD	: Chemical Oxygen Demand
FBC	: Fluidized Bed Combustion
BFBC	: Bubbling Fluidized Bed Combustion
CFBC	: Circulating Fluidized Bed Combustion
TGA	: Thermogravimetric Analysis
TG	: Thermogravimetry
DTG	: Differential Thermogravimetry
DTA	: Differential Thermal Analysis

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LIST OF SYMBOLS

T_{boil} : Boiling point
L_v : Heat of vaporization
η : Furnace efficiency
λ : Excess air factor
E : Activation energy
A : Pre-exponential factor
$f(\alpha)$: Conversion function
k : Reaction rate constant
A : Frequency factor
E : Activation energy
R : Gas constant
b : Constant heating rate
T_o : Initial temperature
α : Conversion
T : Temperature at time t
W_o : Initial weight of the sample
W_t : Weight of the sample at time t
W_∞ : Weight of the sample at the end of the reaction
n : Reaction order
P_v : Vapor pressure
r^2 : Regression coefficient

SUMMARY

In today's world, many developed countries are in the rush of guaranteeing their energy sources for the future. The energy demand of the world is increasing due to increasing population and developing technology. It is expected to have an energy crisis in the next century due to the depletion of the limited fossil fuel reserves. With these conditions, it is vital for countries to use alternative energy resources. Many countries have efforts to partially switch to renewable energy sources like wind, solar, biomass, tidal and geothermal energies.

Some of these energy sources are used today, though they are not very common. The most used one is biomass energy, especially in developing countries.

The share of biomass energy in primary energy consumption of developed countries is below 3 % and in still-developing countries this share changes between 20-90 %. Biomass stands for 15 % of the worlds total energy consumption.

Many European countries, USA, Canada, and Brazil have ongoing projects; working large or pilot scale plants and aims to increase the shares of biomass in their future consumption.

Turkey is a country which imports more than half of the energy it uses. It is estimated that this amount is going to increase. At present Turkey does not make much use of its biomass potential but there is a great opportunity to provide energy from biomass.

Biomass, as a renewable energy source, has economic and environmental advantages. The advantage of keeping the environment cleaner when compared to fossil fuels makes biomass very attractive. The most important environmental effect of biomass is that it does not add up to carbon dioxide emissions because newly grown biomass absorbs the carbon dioxide emitted during combustion. Evaluating biomass as a fuel also provides us the opportunity to avoid land filling and problems with the disposal of wastes.

From an economical view, the option to partially decrease reliance on imported energy sources makes biomass a strategically preferable alternative. In the past, biomass technology was very expensive and could not compete with fossil fuels but with the improvement of technology and increasing research, now biomass combustion systems compete with traditional methods.

The biomass energy systems are considered to produce different energy carriers, namely heat and/or power.

Biomass could be of two types: virgin biomass and waste biomass. Virgin biomass is purpose-grown species and waste biomass is residues from agricultural operations, municipal solid waste (MSW), sewage etc. This variety of species and their different physical properties necessitate the design of specific systems for every type of biomass.

As biomass can't always be converted effectively to energy using direct combustion, some conversion processes are necessary. Some thermal processes that convert biomass into valuable fuel are carbonization, gasification, anaerobic digestion, liquefaction and pyrolysis.

Combustion after some physical operations (drying, size reduction) is the most common method to obtain energy from biomass. Besides using only biomass as a fuel, co-combustion with fossil fuels is also an option.

Drying, pyrolysis and reduction, combustion of the volatile gases and combustion of the char are the four stages of combustion. Fixed-bed and fluidized-bed systems can be used for combustion of biomass. These units produce the heat necessary for the steam cycle which provides power.

Process conditions and biomass properties strictly affect the design of combustors.

In order to design a combustion system for biomasses, the combustion kinetics of the species should be known in detail. Thermogravimetric analysis is the most used technique to achieve this. This method, which could be isothermal or non-isothermal, investigates the behavior of the components of biomass under the analysis conditions.

Important kinetic parameters can be calculated from the thermogravimetric (TG) data obtained, using many different models. In this study Coats-Redfern model was used.

The data for the model have been obtained carrying out experiments with a thermogravimetric analyser. Ten samples of biomass namely as olive bagasse, sunflower shell seed, rapeseed, walnut shell, pine cone, tea residue, cotton bagasse, grape seed, hybrid poplar, and sour cherry stone have been burned with two different heating rates and the resulting TG curves have been used to derive the differential thermogravimetric (DTG) curves. Maximum temperature of combustion, maximum burning rate and combustion time was extracted from the DTG curves. These data was compared with the ultimate, proximate, structural and calorific analyses that were obtained with a research project carried at Chemical Engineering Department, ITU [1].

BAZI TARIMSAL ATIKLARIN İZOTERMAL OLMAYAN DURUMDA YANMA KİNETİKLERİNİN İNCELENMESİ

ÖZET

Günümüzde birçok gelişmiş ülke gelecek yıllar için enerji kaynaklarını garantilemek istemektedir. Sürekli artan nüfusa ve gelişen teknolojiye bağlı olarak dünyada enerji talebi artmaktadır. Fosil yakıt rezervlerinin tükenmeye yüz tutmasından ötürü önümüzdeki yüzyıl içerisinde dünyanın bir enerji darboğazına düşmesi beklenmektedir. Bu şartlar altında ülkelerin alternatif enerji kaynaklarına yönelmeleri kaçınılmazdır. Birçok ülke rüzgar, güneş, biyokütle, gel-git ve jeotermal enerjiler gibi alternatif kaynaklara yönelmiştir.

Günümüzde de bu kaynakların bazıları çok yaygın olmasalar da kullanılmaktadırlar. Biyokütle, bu kaynaklardan özellikle gelişmekte olan ülkelerde en çok tercih edilenidir.

Dünyanın toplam enerji tüketiminde biyokütle'nin payı gelişmiş ülkelerde % 3'ün altında iken gelişmekte olan ülkelerde bu oran % 20 ile % 90 arasında değişmektedir. Dünyada toplam enerji tüketiminin % 15'i biyokütle'den sağlanmaktadır.

Birçok Avrupa ülkesinin yanı sıra ABD, Kanada ve Brezilya'da büyük ya da orta ölçekli ticari ve araştırmaların yürütüldüğü pilot biyokütle tesisleri mevcuttur. Bu ülkelerde biyokütle kullanımının arttırılmasına yönelik hedefler de belirlenmiştir.

Türkiye tükettiği enerjinin yarısından fazlasını ithal eden bir ülkedir. Bu oranın artması beklenmektedir. Türkiye'de günümüz itibariyle biyokütle kaynaklarından yeterince yararlanılmamaktadır; ancak, değerlendirilebilecek ciddi bir potansiyel mevcuttur.

Yenilenebilir bir enerji kaynağı olarak biyokütlenin ekonomik ve çevresel avantajları vardır. Fosil yakıtlara kıyasla temiz bir yakıt olması biyokütle'yi tercih edilir kılmaktadır. En önemli çevresel etkisi karbondioksit çevrimine daha fazla gaz eklenmesine sebep olmamasıdır; çünkü, yeniden büyüyen biyokütle, enerjiye dönüşüm esnasında açığa çıkan karbondioksiti absorblamaktadır. Biyokütlenin enerji kaynağı olarak kullanımı, bu atıkların bertarafı için ayrılacak kaynaklardan da tasarruf sağlar.

Ekonomik açıdan bakıldığında ise fosil yakıt rezervleri yeterli olmayan ülkeler için ithal enerjiye bağımlılığı kısmen azaltabileceği için biyokütle, stratejik bir anlam da kazanmaktadır. Eskiden biyokütle teknolojisi pahalıydı ve fosil yakıtlarla rekabet edebilirliği azdı ancak araştırmalar hızla ilerlemekte olduğundan biyokütle, fosil yakıtlara kıyasla daha ekonomik ve rekabet edebilir bir yakıt olmaya adaydır.

Biyokütle enerjisi buhar, su vb. gibi değişik taşıyıcı ortamlar aracılığıyla taşınarak ısı ya da güç üretilebilir.

Biyokütle, taze biyokütle ve atık biyokütle olarak başlıca iki grupta sınıflandırılır. Taze biyokütle enerji bitkileri olarak da adlandırılan, enerji kaynağı olarak kullanımı

maksadıyla özel olarak yetiştirilen türleri kapsar. Atık biyokütle ise tarımsal atıklar, evsel atıklar ve atık sular gibi kalorifik değeri olan atıklardır. Biyokütle türleri arasındaki bu çeşitlilik, türlere özel sistemlerin tasarımını zorunlu kılar.

Bazı durumlarda biyokütle, direkt olarak yakmayla verimli olarak enerjiye çevrilemeyebilir. Bu nedenle geliştirilmiş başka prosesler de vardır. Bu amaçlı bazı termal prosesler karbonizasyon, gazlaştırma, havasız ortamda sindirim, sıvılaştırma, ve piroliz'dir.

Kurutma ve boyut küçültme gibi bazı fiziksel operasyonlar ardından yakma, biyokütleden enerji elde etmek için kullanılan en yaygın yöntemdir. Tek başına biyokütle yakmak kadar kömür ya da doğal gaz ile beraber yakmak da uygulanan bir seçenektir.

Yakma; kuruma, piroliz ve indirgenme, uçucu gazların yanması ve oluşan kok'un yanması olarak adlandırılan dört aşamadan oluşur. Bu işlem sabit yataklı ya da akışkan yataklı reaktörlerde gerçekleştirilebilir. Bu reaktörler güç üreten buhar çevrimi için gerekli ısıyı sağlarlar.

Yakma sistemi tasarımları biyokütlenin özelliklerine ve proses şartlarına büyük ölçüde bağlıdır.

Bir yakma sistemi tasarlayabilmek için yakılacak biyokütle türünün yanma kinetiği iyi bilinmelidir. Yanma kinetiğini incelemenin en iyi yolu termogravimetrik (TG) analiz yapmaktır. İzotermal ya da izotermal olmayan şartlarda yapılabilen bu analiz, biyokütle bileşenlerinin yakma koşulları altındaki davranışını inceler.

Elde edilecek olan termogravimetrik verilerden değişik matematiksel modeller kullanılarak kinetik parametreler hesaplanır. Bu çalışmada Coats-Redfern modeli kullanılmıştır.

Model için gerekli veriler on farklı biyokütle türünün termogravimetrik analiz cihazıyla yürütülmüş deneylerinden elde edilmiştir. Bu numuneler sırasıyla zeytin küspesi, ay çekirdeği kabuğu, kolza tohumu, ceviz kabuğu, çam kozalağı, çay atığı, pamuk atığı, üzüm çekirdeği, melez kavak ve vişne çekirdeğidir.

Numunelere iki farklı ısıtma hızı uygulanmış ve elde edilen TG eğrilerinden diferansiyel termal gravimetri (DTG) eğrileri türetilmiştir. Maksimum yanma sıcaklığı, maksimum yanma hızı ve yanma süresi bilgileri DTG eğrilerinden elde edilmiştir. Bu veriler İTÜ Kimya Mühendisliği bölümünde yapılmış olan bir araştırma sonucu elde edilmiş olan biyokütle numunelerine ait elementer, kısa, kalorifik ve yapısal analiz sonuçlarıyla kıyaslanmıştır [1].

1. BIOMASS

1.1. Definition

Biomass is plant matter such as trees, forest residues, grasses, agricultural crops and agricultural wastes or other biological material like animal wastes and municipal solid waste [2]. It can be used as a solid fuel, or converted into liquid or gaseous forms. With conversion processes like carbonization, gasification, combustion and co-firing, pyrolysis, anaerobic digestion, liquefaction and some other processes, biomass can be converted into fuels like ethanol and renewable diesel, electricity, heat, chemicals (plastics, solvents, pharmaceuticals, chemical intermediates, adhesives, furfural, fatty acids, acetic acid, carbon black, paints, dyes, pigments, ink and detergents), food and feed [3, 4].

1.2. Importance

The prospect of producing clean, sustainable power in substantial quantities from biomass is a growing interest worldwide, stimulated by increasing concern over the environmental and economical consequences of conventional fossil and nuclear fuel use.

The usage of biomass as fuel has environmental and economic advantages. In general the benefits are reducing:

- Net emissions of CO_2, NO_x and SO_2 during power production
- The demand for fossil fuels
- The volumes of biomass material committed to landfill [5, 6].

1.2.1. Economic advantages

Renewables and nuclear power are the major alternatives to fossil fuels at present. With time, renewables as a source for energy production will become even more important as the reserves of fossil fuels diminish and finally fade out. Biomass, wind, wave, tidal and direct solar energy are all renewable energy sources with a future

potential far beyond their use today. They are in general, more evenly dispersed over the earth's surface than fossil fuels or uranium. The renewable energy sources thus increase the possibilities for local, regional or national energy self-sufficiency and decrease the reliance on imported energy.

Biomass is easy to find and readily available everywhere and with the recent developments of technology to use it efficiently with low levels of emissions make it a more attractive fuel option [2].

Biomass combustion has the potential to meet future demands but variability in properties of biomass fuels is large and these may influence the efficiency and environmental impacts associated with its utilization [7].

Through photosynthesis organic matter with energy content of about $3*10^{21}$ J is produced each year. The global commercial energy use of today is about ten times less and the food energy consumption is about 200 times less than that. This means that there is a considerable unused potential for energy production by the use of biomass through combustion, gasification and other conversion techniques, both for heating purposes, electricity production and for liquid fuel production [8].

At present, in many countries key problems regarding the use of available biomass residues for energy production are the high costs of the technology compared to fossil fuels. Therefore, an optimization for a maximum of energy production at minimal costs is desired. The large number of possible combinations of various biomass streams, conversion options, scale ranges, logistics and energy carriers produced, makes it difficult to identify optimal systems [9].

1.2.2. Environmental advantages

As a source of energy, biomass has good and bad effects on the environment. Good effects are that it is a renewable energy that has low sulfur and relatively low ash content and zero net CO_2 as the CO_2 emitted is absorbed with the growth of new biomass [2, 10, 11].

Biomass also contributes to soil fertilization and stabilization, improves physical properties of soil, and reduces water run-off and desertification [12].

Wood for example, as a biomass fuel, has several advantages over coal: it possesses much lower contents of sulfur and heavy metals and it generates an ash that may be

returned to the soil as fertilizer [13]. Besides, firewood is obtained from local sources and if only dead and useless trees are used, no forests are lost [2].

The conversion of organic wastes into fuel reduces the environmental hazards and costs associated with the disposal of these wastes.

Another fact is that the removal of agricultural residues from soil means removing the nutrients that should return to soil as fertilizer but the residues of production of energy from agricultural biomass processes also can be used as a fertilizer.

One of the conversion methods namely as pyrolysis provides means for efficient and economical conversion of residues which themselves are major sources of pollution.

A bio-fuel methanol has been regarded as an excellent fuel because it burns very well, can be readily transported and stored. Methanol has a high heat of vaporization compared to gasoline and this results in lower combustion temperatures and less formation of NO_x.

The mixture of 66 % methane and 33 % carbon dioxide with 1 % of hydrogen, nitrogen, organic sulfides and hydrocarbons is known as biogas. Agricultural and agro-industrial residues and animal manure can be converted into fuel in anaerobic digestion. This is important for places where proper disposal systems are not present. Manure is a source of different parasites and its useful disposal prevents people from parasitic diseases and using these wastes as a source of energy avoids both the hazard and the disposal cost.

On the other hand, biomass usage has some disadvantages, too. Biomass burning is widespread, especially in tropics and serves to clear land for shifting cultivation, to convert forests to agricultural and pastoral lands, and to remove the vegetation in order to promote agricultural productivity and the growth of high yield grasses. It is an important source of trace gas emissions, aerosols and has important effects on atmospheric chemistry and the radiation budget. Trace gases contribute to the green house effect. Biomass burning has considerable effects on the characteristics of the atmosphere and consequently on regional and global climate [3].

Fermentation produces alcohol as a fuel but the effluents contain components that could damage the environment.

Depending on the fuel composition, the design of the combustion device and the operation of the system, the combustion of biomass can lead to many emissions. Unburnt pollutants (CO, HC, tar, PAH and unburnt particles) and oxidized pollutants (NO_x, CO_2 and in certain cases N_2O) originate from all types of biomass. HCl, SO_2 and salts originate from biomass containing Cl and S; urban waste wood, demolition wood and short rotation biomass like straw, grass etc.

Ash particles originate from all types of biomass and absorb most of the sulfur content of the biomass. Heavy metals (Pb, Zn, Cd, Cu, Cr etc.) originate from biomass containing these. Dioxins are emitted by all types of biomass; in low concentrations from native biomass (low Cl content) and in higher concentrations from urban waste wood and demolition wood (high Cl content).

Unburnt pollutants originate from incomplete combustion and can be reduced effectively if the combustion air, especially the secondary air, is mixed homogeneously at an optimum fuel/air ratio with the combustible gases and burnout takes place at a high combustion temperature with sufficient residence time.

Oxidized pollutants such as NO_x originate mainly from the fuel bound nitrogen. Two types of NO_x formation take place during combustion: thermal NO_x formation (above 950°C, nitrogen in the air is oxidized) and fuel NO_x formation (due to nitrogen content of fuel) at lower temperatures [2]. Thermal NO_x is of minor importance since the combustion temperature is usually below the limit. For the reduction of NO_x, both primary and secondary measures can be taken [8].

1.3. Laws and Regulations

Currently, political pressures in the form of European renewable energy targets, atmospheric carbon quotas and other emissions limits are added incentives to reduce fossil-energy consumption. Although technical factors including the typically low heating value of biomass compared with coal make it unfeasible to rapidly switch to biomass energy, the recent European energy policies are strongly encouraging the use of biomass for energy purposes, mainly owing to three targets: economic and social development of countryside, elimination of wastes and reduction of CO_2 emissions [14].

In order to reduce CO_2 emissions from fossil fuel combustion, Danish power plants are obliged to utilize annually at least 1.0 million tones of straw by the year 2004 [4].

The International Energy Agency (IEA) has provided a framework for the co-ordination of research on bioenergy technologies for over thirty years now. The purpose is to increase co-operation among those in the field of bioenergy. The combustion activity started between Canada, Denmark, Finland, Italy, The Netherlands, Norway, Sweden, Switzerland, Austria, USA, and UK. Work groups had been organized to study on emissions and fuel activity [8].

In USA, there are regulations both for using biomass as a fuel and also to use more efficient burning systems. There are also tax incentives for dedicated investments.

The importance of biomass burning is well recognized in International Global Atmospheric Chemistry (IGAC) and one of the initial IGAC activities, Biomass Burning Experiment (BIBEX): Impact on the Atmosphere and Biosphere [15].

In Turkey, the "Renewable Energy Law" which is expected to support investments in this sector has been approved in May 2005.

1.4. History

For thousands of years, biomass, especially wood has been the domestic heating fuel, and in isolated situations sufficient amounts of power are still generated by burning local forms of biomass.

After the industrial revolution, petroleum based fuels have been important and most of the study of technology was on the efficient usage of these. Some countries that did not have reserves in their land were obliged to import fuel.

After the petroleum crisis in 1973, alternative energies have become popular and since then renewable energy technologies have advanced a lot. The industrialized countries still use petroleum, natural gas and coal. But this era is to end too when someday fossil fuels will deplete and not be sufficient for supply. Biomass with its developing technologies will be the main source of energy again [16].

1.5. Types

Waste biomass and purpose-grown virgin biomass are the two alternative groups of bio-fuels for biomass conversion processes.

1.5.1. Virgin biomass

Since at least 250,000 botanical species, of which only about 300 are cash crops are known in the world. But compared to total known species, a very small number of them are suitable for the manufacture of synfuels and energy products. The selection is not easy due to the many parameters related to biomass. Some of these are growth area availability, soil type, quality and topography, propagation and planting procedures, growth cycles, fertilizer, herbicide, pesticide and other chemical needs, disease resistance of monocultures, insolation, temperature, precipitation and irrigation needs, pre-harvest management, crop management, harvesting methods, storage stability, drying methods, other possible uses of the plant and the possibility of growing more than one species for sequential use and transportation.

The biomass selected should be of high-yield with low cash value, short growth cycles and a good adoption to the soil where the system is to be built. Plants should not require too much fertilizer and should fix ambient nitrogen, not requiring too much external nutrients. In places where annual rainfall is not much, they should be able to live with little water. Terrestrial crops should grow well on poor soils and after harvesting; they should grow again without the need to plant again.

Virgin biomasses are divided into two groups that are terrestrial biomass and aquatic biomass [3].

1.5.1.1. Terrestrial biomass

Terrestrial biomasses are forest biomass, grasses and other cultivated crops.

About one third of the world's land area is forestland. There are exploitative, conventional extensive, conventional intensive, naturalistic and short rotation methods to grow trees. These trees are hundreds of species in the seven genera Acacia, Casuarina, Eucalyptus, Pinus, Prosopis and Trema.

Eucalyptus is a rapidly growing tree and has gathered many of the attention as a biomass source. Because of its properties, it is the first candidate to be grown for

energy usage. Various species and hybrids of the genus Populus are also of importance as SRWC (Short Rotation Woody Crop) growth.

Grass is a family that includes about 400 genera and 6000 species some of which are the great fruit crops, wheat, rice, corn, sugarcane, sorghum, millet, barley, oats, clovers, alfalfa and such crops. These grasses are candidates for conversion to synfuels.

Some terrestrial biomass types are proposed especially for energy usage and some like sugarcane have multiple uses. Sugarcane grows rapidly and has a high yield. The fibrous bagasse is used as boiler fuel in many sugar factories and sugar derived ethanol is used as a motor fuel in gasoline blends, namely as gasohol.

Switchgrass is also recommended as a commercial energy source. It has a high growth rate, adapts to marginal sites and tolerates water and nutrient limitations.

Other perennial grasses are reed canary grass, tall fescue, wheatgrass, weeping lovegrass and Bermuda grass.

Besides forests and grasses, there are cultivated crops which can also be considered for energy purposes. These are kenaf, sunflower, buffalo gourd, alfalfa, soybean, and rapeseed.

1.5.1.2. Aquatic biomass

Aquatic biomasses exhibit higher net organic yields than terrestrial biomass. Algae, freshwater plants and marine species belong to this group.

Unicellular algae like Chlorella and Scenedesmus can be produced at high yield at outdoor light. The nutrients for algae production can be supplied with municipal biosolid or other wastewaters. The high water content of algae tends to limit the thermochemical conversion process and it is preferable to use biological methods.

Macroscopic algae like Giant Brown Kelp and other seaweeds are also considered as a renewable energy source. They are also sources for producing organic gums, thickening agents and alginic acid derivatives.

Among the water plants, water hyacinth is productive and is the primary candidate to be marine source of renewable energy. It doesn't have other commercial uses and it is not desired in waterways [3, 17].

1.5.2. Waste biomass

Waste biomass includes municipal wastes (MSW, biosolids), agricultural solid wastes (livestock and poultry manures, agricultural crop residues), forestry residues and industrial wastes.

1.5.2.1. Municipal wastes

Municipal wastes are mainly MSW (garbage) and biosolids (sewage, sludge).

Disposal of MSW in big cities is getting more and more expensive each year. MSW disposal by conventional methods is also a loss of natural sources as it has combustible components and land is lost due to landfilling. Energy potentially available from MSW in USA in 1990's was 2.5 EJ/year. The importance of combined waste disposal and energy recovery is evident.

The disposal of MSW has become an increasingly costly problem because of the decrease in space available for landfills and growing concern about the living environment. Typical MSW in an industrialized country contains 28 % paper, 7 % cellulosic cloth, 4 % yard waste, 27 % food waste, 15 % plastics, 1 % leather and rubber, 6 % metals, 6 % glass, 1 % ceramic and 5 % miscellaneous wastes.

Because of its advantage of maximum volume/quantity reduction and energy recovery, MSW incineration has been resorted to in more and more cities [18]. MSW is combusted as received or with some processing to reduce particle size and to separate some of the recyclable components like paper, aluminum, iron, batteries, glass etc.

MSW is either burned as it is or grinded to smaller particles after the separation of some basic materials. Mass burn systems usually have water walled combustors, refractory covered furnaces and rotating burners. Modular systems are used to burn smaller amounts of MSW and have multiple smaller combustor units [3].

Coated printing and writing paper is one of the principle materials contributing to the MSW. Such waste paper has a calorific value of 11 MJ/kg, its conversion to fuels is a worthy goal and an environmental standpoint [19].

Biosolids are wastewaters from residential sources, industry and ground water infiltration. The pollutants in these sources are very toxic and contain pathogenics. The main purpose of wastewater treatment is to remove these pollutants and balance

the wastewater with the receiving water. Biosolids have an annual energy content of about 0.114 EJ in USA.

1.5.2.2. Agricultural solid wastes

Agricultural solid wastes are animal wastes and agricultural crop residues. Energy potential of animal excreta is about 4.6 EJ/year in USA. Farms where cattle, hogs, pigs, sheep and poultry live are potential places to obtain this input.

Agricultural crop residues are those left in the field or accumulated during sorting and cleaning of the products like soybean, corn, wheat, barley, rice and sorghum. These could be returned to soil, could be used as animal feed and could be used for energy generation. It is estimated that these crop wastes have an energy potential of 4.2 EJ/year in USA [13].

1.5.2.3. Forestry residues

Forestry residues are the pieces left on forest floor after some logging operations like cutting off stems, roots, bark residues and damaged trees etc. It is known that most of the forest residues are wasted [13, 20].

Wood consists of cellulose, hemicellulose and lignin, which in different fractions are also the major components of wood based products. Cellulose, however, is often the major constituent. Hemicellulose has a chemically complex structure, containing a number of polymeric components like xylans, galactans and mannans. In the literature, xylan is commonly used to substitute hemicellulose but one should be aware that xylans represent only one type of celluloses [21].

Wood also contains extractives like terpenes, tannins, fatty acids, resins and water and mineral matter. Its composition varies in species and within the same species it varies with the habitat, age and location in the tree (trunk, branches, roots etc.) [22].

1.5.2.4. Industrial wastes

A general trend of recycling can be observed in the pulp and paper industries. They and food processing industries generate great amounts of waste biomass. Pulp and paper industries use their black liquor of the process as fuel. This is the sludge generated during the de-inking process. The sludge contains fiber, ink, pigments and clay fillers, as well as enough combustibles to be considered as a low-grade fuel.

However, it may also contain both carcinogenic/mutagenic aromatic hydrocarbons and toxic metals [3, 23, 24].

Rice husk, as an agricultural residue, constitutes the largest (about 20 %) and most useless by-product of the rice milling industry [6].

Press mud is an industrial waste available from the sugar mills. Press mud has about 68 –70 % of moisture, 24-28 % of combustibles and 6-8 % ash. Dry press mud has higher percentage of combustibles which could be used for energy generation [25].

Scrap tires accumulated in stockpiles or uncontrolled dumps can cause serious problems to the environment, public health and safety. The piled tires provide breeding sites for mosquitoes that can spread serious diseases and are vulnerable to cause fire hazards. Since rubber materials are essentially non-biodegredable, they are not suitable either for compost or landfilling. Accordingly, thermal treatment by pyrolysis or incineration of these materials is attractive [26].

1.6. Properties of Biomass

The chemical composition of biomass varies among species, but biomass consists of about 25 % lignin and 75 % carbohydrates or sugars. Most species also contain around 5 % of smaller molecular fragments, called extractives. The carbohydrate fraction consists of many sugar molecules linked together in long chains or polymers. Two larger carbohydrate categories that have significant value are cellulose and hemicellulose. The lignin fraction consists of non-sugar type molecules linked together in large two dimensional mesh structures. The lignin binds the cellulose fibers together [27].

Each type of biomass has specific properties that determine its performance as a fuel in combustion or gasification devices. The most important properties are moisture content, ash content, volatile matter composition, elemental composition, heating value and bulk density. These can be expressed on wet basis, dry basis and dry and ash free basis. The proportions of moisture, ash and ash free matters are critical in evaluating the suitability of biomass as a fuel.

Biomass materials exhibit a wide range of moisture content; from less than 10 % in cereals to 50-70 % in forest residues on a wet basis.

The inorganic matter (ash) content can vary from less than 0.5 % in wood to 30-40 % in rice husks.

The total ash content and its composition are important for the performance of combustor and gasifier systems.

Volatile matter refers to the part of the biomass that is released when the biomass is heated up to 400-500°C. During the heating, decomposition into volatile gases and solid chars occur. Biomass typically has an 80 % volatile matter content.

The composition of the ash free organic component of biomass is relatively uniform. The major components are carbon, oxygen and hydrogen. Most biomass also contains a small amount of nitrogen and sometimes chlorine and sulfur.

The heating value of the fuel is an indication of the energy chemically bound in the fuel. It is expressed in heating value (J) per amount of matter (kg). There are higher and lower heating values, which mean the reference state of water is liquid, and the reference state of water is vapor, respectively.

Biomass always contains some water which is released as vapor upon heating. This means that the evaporation process absorbs some of the heat generated during chemical reactions. The maximum allowable moisture content must be 55 % to be able to ignite and extract energy from the fuel.

Table 1.1: Comparison of some properties of selected biomass [2]

Type	LHV (kJ/kg)	Moisture Content (%)	Ash Content (%)
Bagasse	7.700-8.000	50	1,7 - 3,8
Cocoa Husks	13.000-16.000	8	11
Coconut Shells	18.000	8	4
Coffee Husks	16.000	10	0,6
Cotton Residues	16.000	15	0,1
Maize	13.000-15.000	15	2
Palm Oil Residues			
Fruit Stems	5.000	63	5
Fibers	11.000	40	-
Shells	15.000	15	-
Rice Husk	14.000	9	19
Straw	12.000	10	4,4
Wood	8.400-17.000	30	0,25 - 1,7
Charcoal	25.000-32.000	5	0,5 - 6

In Table 1.1, lower heating values, moisture and ash contents of some biomass types are given for comparison.

Bulk density refers to the weight of material per unit of volume. This value changes from 150-200 kg/m^3 in cereals to 600-900 kg/m^3 in solid wood.

Heating value and bulk density together determine the energy density of the biomass. That means the potential energy available per unit volume of biomass. In general, biomass has a density as much as one tenth of coal [2].

Size and shape of biomass is an important value. The greater the overall surface area of fuel exposed to the required quantities of oxygen and heat, the faster the burning process will occur and hence the greater the power output will be. That is why size reduction is preferred in most types of biomass.

On the other hand, many biomass species like sawdust are used in briquette or pellet forms that increase their size and reduce the overall area. This provides them slower burning process and easier handling [12].

Pellets are a refined, solid fuel biomass with low moisture content, which makes it easy to transport, store and convert into energy. It is manufactured from sawdust, wood chips, shaving or bark. Pellets are typically 6-8 mm in diameter and 5-30 mm long. The maximum water content is 8 %.

The following list contains the main advantages of using pellets:

- Pellets burns almost without any smoke development.
- Less carcinogens are produced in the high temperature combustion of pellets compared with unrefined fuel.
- It has a low heavy metal content.
- Only small quantities of NO_x are formed.

Biomass is usually processed to pellets in plants using piston or roller presses. The raw material used may be sawdust, shavings or chips. The raw material is heated, to make the fuel dry and at the same time transforming the lignin acting like the glue that holds the raw material together, which makes it possible to shape the pellets in the desired form [24].

2. TECHNOLOGIES TO OBTAIN ENERGY FROM BIOMASS

A few types of biomass like fuel wood may be used directly as fuel, by means of direct combustion. However, most types of biomass require some conversion before being used as fuel. The purposes of conversion are that biomass only has a modest thermal content compared to fossil fuels, has a high moisture content which inhibits combustion, has a low bulk density which requires very large equipment for handling, storage and burning and its physical form is not homogenous and free flowing. The conversion processes involve the drying of biomass and improving its handling characteristics with turning it into a fluid (gas or liquid).

Besides the physical conversion processes like drying and size reduction, there are thermal conversion processes that are carbonization (charcoal production), pyrolysis (pyrolytic oils production) and gasification (producer gas production) and the biological conversion processes are anaerobic digestion (biogas production) and liquefaction (ethanol and methanol production). A summary of these processes is given in Figure 2.1 [3, 5].

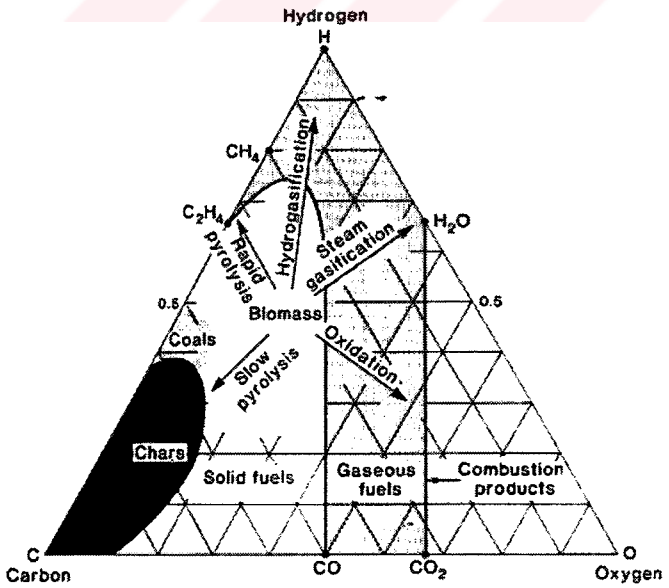

Figure 2.1: Summary of thermal conversion processes [5]

2.1. Direct Combustion

The direct combustion of biomass to produce heat is the simplest way to utilize the material. But this method is inefficient because there is no moisture reduction, the thermal yield is low and it is hard to handle.

In industrial scale, direct combustion is achieved with water-tube boilers. This device has a large combustion area surrounded by banks of vertical tubes. Because the biomass fuels have a high content of volatile matter and lower density and bulk density compared with solid fossil fuels, they need larger areas for combustion.

At present biomass is converted into electricity most often by direct combustion, followed by a steam cycle. Large scale (>10 MW) power plants are in operation mainly in countries such as USA, Denmark, Sweden, and Finland [3].

Detailed information on combustion will be given in Chapter 3.

2.2. Carbonization

Charcoal is produced by means of carbonization. This is a process where wood is heated with limited airflow resulting in the production of charcoal and other liquid and gaseous by-products.

The four stages of carbonization are as follows: the first stage is endothermic and involves the initial drying of the wood to be carbonized (up to 473 K). The second is the pre-carbonization stage, also endothermic and pyroligneous liquids like methanol, acetic acid, CO and CO_2 are formed (443-573 K). The third stage, which is exothermic, involves the production of charcoal by the release of the light tars and pyroligneous acids (523-573 K). The final stage involves the release of the remaining volatile components of the charcoal increasing the carbon content (above 573 K).

The key chemical reaction is:

$$C_{6n}(H_2O)_{5n} \rightarrow 6n\ C + 5n\ H_2O \qquad (2.1)$$

typical biomass — carbon — moisture

Secondary reactions are:

$$C + H_2O \rightarrow CO + H_2 \quad (2.2)$$

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 \quad (2.3)$$

$$C + 2H_2 \rightarrow CH_4 \quad (2.4)$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \quad (2.5)$$

The moisture content, the chemical composition of wood and the carbonization temperature affect the carbonization yield. Earth kilns, metal kilns, brick kilns and cement kilns are the types of kilns for carbonization [12]. Below is the picture of a brick kiln.

Figure 2.2: Brick kiln [28]

2.3. Gasification

Besides combustion process, gasification constitutes an attractive alternative to the use of biomass as a fuel. Gasification is the thermal conversion of organic materials at elevated temperature and under various gaseous atmospheres to produce primarily permanent gases, with char, water, and condensables as minor products [5, 14].

The production of a gaseous fuel from solid fuel has many attractions like easy handling, combustion that produce less excess air and low levels of contaminants [2].

Gasification technologies produce gas able to be directly used in internal combustion engines, such as spark ignition ones or gas turbines, for mechanical energy production. One of the main advantages of gasification is the possibility to install small, low-cost and efficient gasifier-engine couples, which permits biomass wastes to be used in situ, and thus, to eliminate much of their cost, such as that derived from storage and transportation to power plants [14].

The gasification product is called producer gas and it consists of 29 % CO and 63 % N_2. Producer gas is used as the fuel for heating purposes, in spark ignition systems and in compression ignition systems. In fluidized beds, it is also possible to produce syngas which consists of CO and H_2. Typical producer gas composition is seen in Table 2.1. Combustible solids are converted to producer gas. The usage of air instead of pure oxygen reduces the temperature due to the diluting effect of nitrogen and cheaper material will do. But in this case slight formation of NO_x occurs and the resulting gas has a lower calorific value because of its nitrogen content [12].

Table 2.1: Typical producer gas composition [12]

Compound	%
CO_2	3,0
C_xH_y	<0.1
O_2	0,9
CO	28,7
H_2	3,8
CH_4	0,2
N_2	63,0

The combustion reaction is:

$$C + O_2 + 3.79\ N_2 \rightarrow 3.79\ N_2 + CO_2 \quad \text{Exothermic reaction} \tag{2.6}$$

The reduction reaction is:

$$CO_2 + C + 3.79\ N_2 \rightarrow 3.79\ N_2 + 2CO \quad \text{Endothermic reaction} \tag{2.7}$$

The main reaction:

$$2C + O_2 + 3.79\ N_2 \rightarrow 3.79\ N_2 + 2CO \quad \text{Exothermic reaction} \tag{2.8}$$

Gasification looks simple in principle and there are many types of gasifiers. For gasification, there are many reactants and many possible reaction pathways. These make the process complex and hard to control and operate [2].

2.3.1. Gasifier types

There are mainly three types of reactors that convert solid biomass to producer gas: updraft or countercurrent gasifiers, downdraft or co-current gasifiers and fluidized bed gasifiers.

2.3.1.1. Updraft or counter-current gasifiers

The biomass is fed at the top and moved downward as a result of its conversion and removal of ashes. Air is taken at the bottom and gas leaves at the top. The biomass passes through drying, distillation, reduction and heart zones. In the drying zone, the biomass is dried. In the distillation zone, it is decomposed into volatile gases and solid char. In the reduction zone, many reactions occur in which carbon is converted into CO and hydrogen is produced as the main component of the producer gas. In the heart zone, the remaining char is combusted, providing heat, CO_2 and water vapor (Figure 2.3).

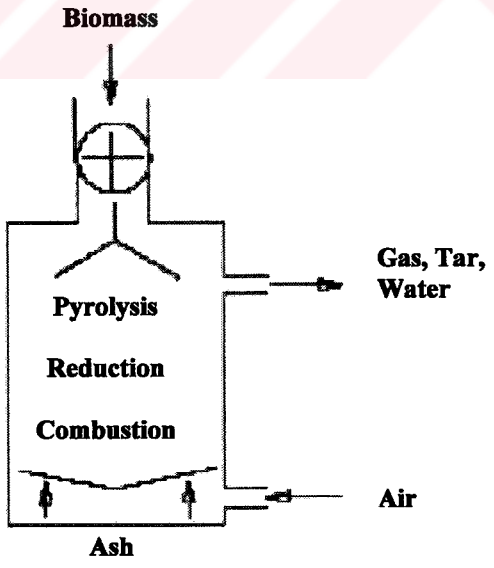

Figure 2.3: Updraft gasifier [5]

2.3.1.2. Downdraft or co-current gasifiers

Biomass is fed at the top and air intake is at the bottom. Gas leaves at the top. Biomass is dried in the drying zone and pyrolyzed in the distillation zone. After the oxidation zone, the remaining char and the combustion products (CO_2 and water vapor) pass to the reduction zone where CO and H_2 are formed (Figure 2.4).

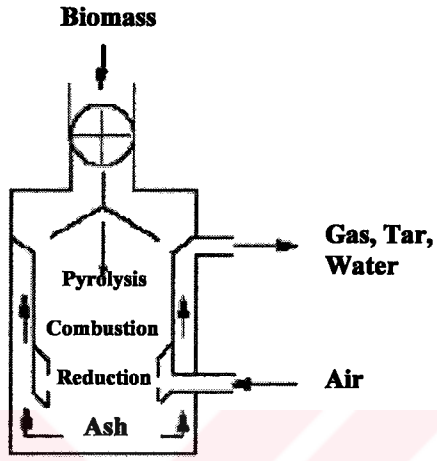

Figure 2.4: Downdraft gasifier [5]

2.3.1.3. Fluidized bed gasifiers

These are designed to gasify fine materials with low bulk density like the rice husk. The fuel is fed into a suspended or circulating hot sand bed. The bed behaves like a fluid and is characterized by high turbulence. Fuel particles mix quickly with the bed material, resulting in rapid pyrolysis and a relatively large amount of pyrolysis gases [2, 12]. This gasifier is seen in Figure 2.5.

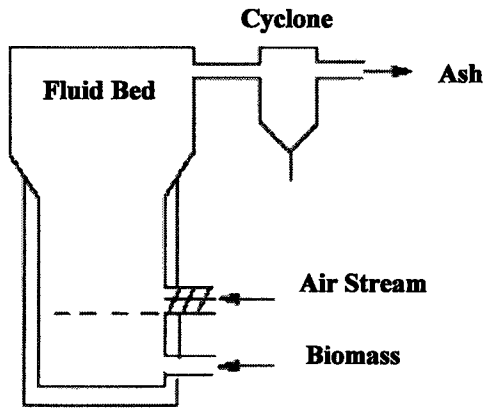

Figure 2.5: Fluidized bed gasifier [5]

The comparison of some gasifiers is given in Table 2.2.

Table 2.2: Comparison of gasifiers [5]

Gasifier	Advantages	Disadvantages
Updraft	Small scale applications Can handle high moisture No carbon in ash	Feed size limits High tar yields Scale limitations Producer gas Slagging potential
Downdraft	Small scale applications Low particulates Low tar	Feed size limits Scale limitations Producer gas Moisture sensitive
Fluidized Bed	Large scale applications Feed characteristics Direct/indirect heating Can produce syngas	Medium tar yield Higher particle loading

2.4. Anaerobic Digestion

Biogas is produced by anaerobic digestion. Biogas contains about 60 % methane, 35 % CO_2 and 5 % a mixture of hydrogen, nitrogen, ammonia, hydrogen sulfide, CO, oxygen, volatile amines and water.

The bacterial decomposition takes place in three stages: hydrolysis phase, acid phase and methane phase. Hydrolysis phase is the breakdown by enzymes of large molecules into smaller ones which can pass through bacteria membrane. During the acid phase, complicated molecules like proteins, fats and carbohydrates are broken down by acid forming bacteria to organic acids, CO_2, hydrogen and ammonia. In the final phase, hydrogen and CO_2 yield some methane and the fermentation of acids and alcohols continues to form methane.

The typical reactions for cellulose are:

Hydrolysis:

$$(C_6H_{10}O_5)n + H_2O \rightarrow n(C_6H_{12}O) \qquad (2.9)$$

Acid phase:

$$(C_6H_{12}O_6) \rightarrow 2\ CH_3CH(OH)COOH \quad (2.10)$$

Methane phase:

$$4H_2 + CO_2 \rightarrow 2H_2O + CH_4 \quad (2.11)$$

$$CH_3CH_2OH + CO_2 \rightarrow CH_3COOH + CH_4 \quad (2.12)$$

$$CH_3COOH \rightarrow CO_2 + CH_4 \quad (2.13)$$

$$CH_3CH_2CH_2COOH + H_2O + CO_2 \rightarrow CH_3COOH + CH_4 \quad (2.14)$$

In a biogas plant all three phases occur simultaneously and if one of them dominates, methane production is seriously affected.

Biogas plants can be of two types: floating gasholder (Figure 2.6) and fixed dome digester (Figure 2.7). In the first one the gasholder is combined with the digester whereas in the second one they are separated [12].

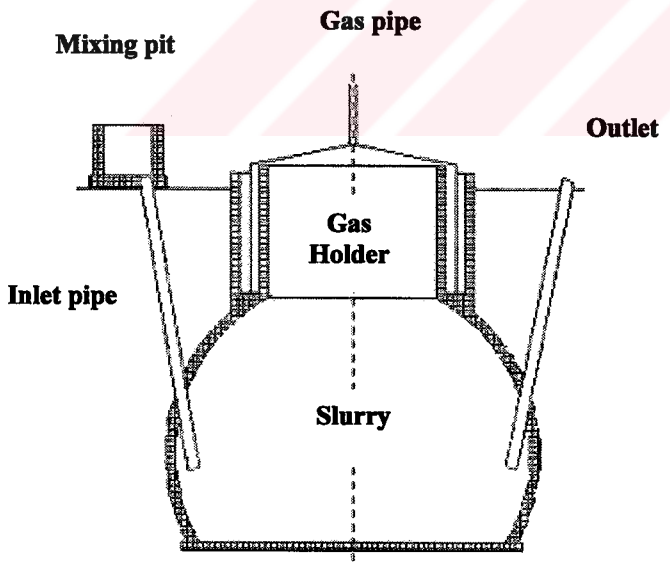

Figure 2.6: Floating gasholder digester [29]

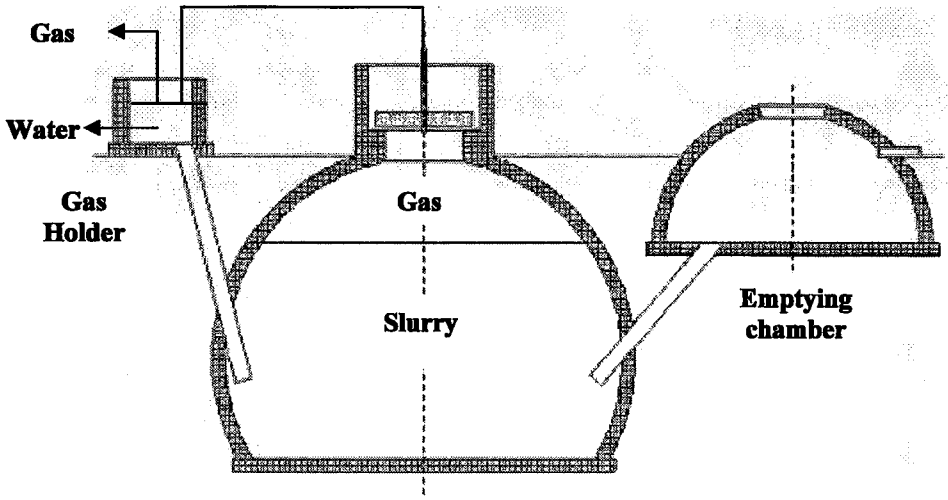

Figure 2.7: Fixed-dome digester [29]

2.5. Liquefaction

Alcohol fuels can be obtained by liquefaction and be used in internal combustion engines directly or blended with gasoline.

Ethanol, for example, is produced with the steps of pretreatment of the feedstock, fermentation and ethanol distillation. In starch containing materials pretreatment process also includes hydrolysis of starch molecules into fermentable sugar. After the batch fermentation of the yeasts, ethanol solution is distilled to a concentration of 95 %. If it is to be added to gasoline, it is concentrated to 99.8 % ethanol.

Sugarcane, molasses, starches like corn, and cellulose like wood and agricultural residues are preferred for ethanol production as a fuel.

Alcohol can also be concentrated using molecular sieves, crystallization and reverse osmosis.

Methanol is another option for alcohol fuels. It is produced from wood and agricultural residues. In the production process, first the material is converted into a gaseous intermediate from which methanol can be synthesized and then methanol synthesis occurs.

The properties of alcohol fuels compared with gasoline are given in Table 2.3.

Table 2.3: Properties of alcohol fuels vs. gasoline [12]

Property	Unit	Fuel Alcohols		Gasoline
		Ethanol	Methanol	
Density	kg/m^3	789	793	735
GCV	MJ/kg	29,7	22,3	46,47
NCV	MJ/kg	27	19,7	43,8
Stoc. Air/Fuel	kg/kg	9	6,5	14,6
T_{boil} (1 bar)	°C	78,5	65	30,2
L_v	kJ/kg	-	1100	400
P_v at 38 °C		-	32	62-90
Viscosity	stoke	-	0,58	0,6
Octane number		106	112	95
Motor		89	91	86

Vegetable oil fuels can also be used as fuel. All vegetable oils have more or less the same properties and the properties of sunflower oil are compared with diesel fuel in Table 2.4 [12].

The process of alcohol fuel production is seen in Figure 2.8.

Table 2.4: Properties of sunflower oil vs. diesel fuel [12]

Properties	Unit	Diesel Fuel	Sunflower Oil
Gross heat value	MJ/kg	45,93	39,38
Specific gravity	kg/m^3	0,84	0,93
Viscosity (37,8 °C)	mm^2/s	3,9	34,7
Octane number		47	37
Flash point	°C	55-77	321
Cloud point	°C	-0,6	-6,6
Carbon residue	%	0,15	0,42
Ash weight	%	0,01	0,04
Distillation 90%	°C	335	335
Sulfur	%	0,27	0,12

2.6. Pyrolysis

Pyrolysis is thermal conversion (destruction) of organics in the absence of oxygen.

The primary products can be mainly gas, liquid and solid depending on the process employed. Most of the projects are interested in the liquid products due to their high energy density, easier storage opportunity and the potential for oil substitution.

Fast pyrolysis is a thermal process that rapidly heats biomass to a carefully controlled temperature (~773 K), then very quickly cools the volatile products (<2 sec) formed in the reactor. Fast pyrolysis occurs at moderate temperature with short residence times yielding 75 % liquid products, 12 % solid char and 13 % gaseous products [5].

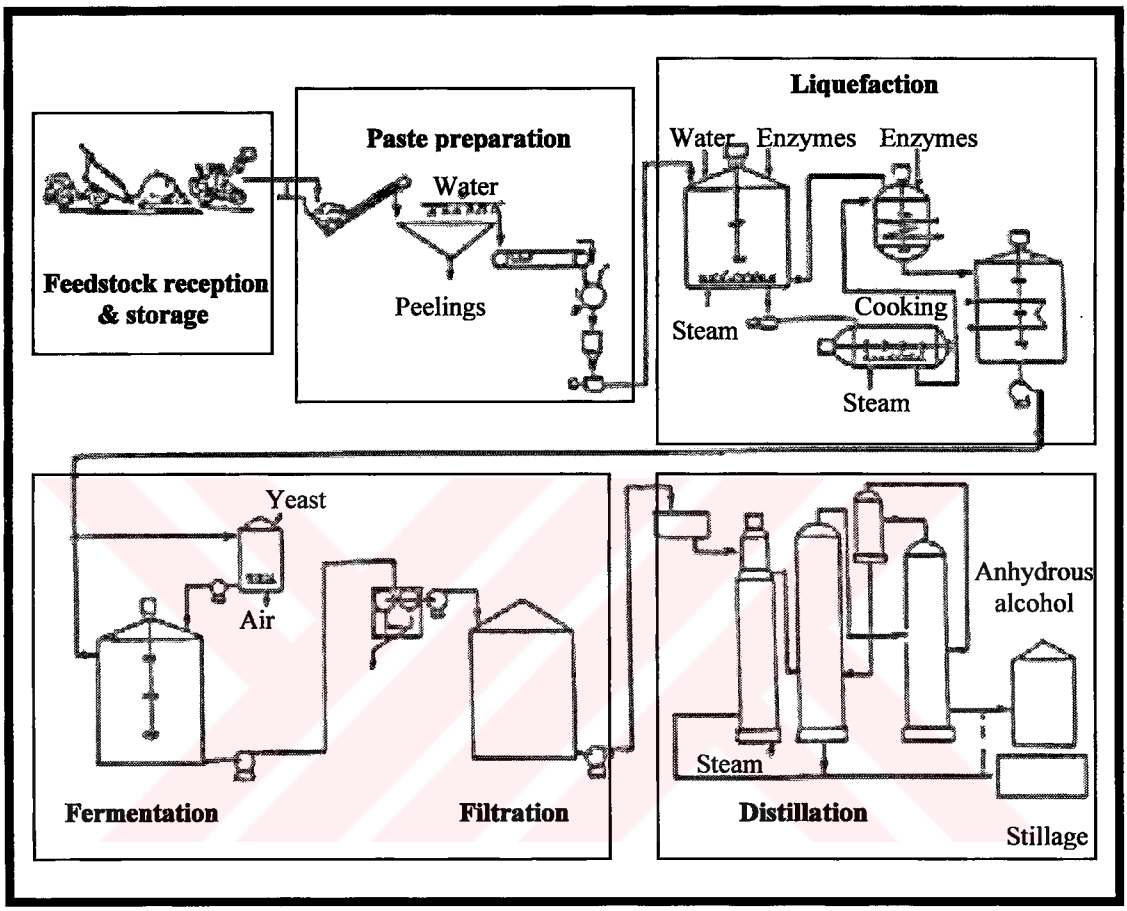

Figure 2.8: Alcohol fuel production [12]

The liquid, when formed, approximates to biomass in elemental composition with a slight GCV of 20-25 MJ/kg, and is composed of a very complex mixture of oxygenated hydrocarbons. The complexity arises from the degradation of lignin, and the broad spectrum of phenolic compounds. The liquid is often called oil, but is more like tar. This also can be degraded to liquid hydrocarbon fuels. The crude pyrolysis liquid is a thick black tarry fluid with up to 20 % wt water and viscosity as heavy oil.

The solid products from pyrolysis process is char, which has limited application in developed countries for metallurgical and leisure use [12]. Char acts as a vapor

cracking catalyst so rapid and effective removal is essential. Using cyclones is the usual method of char removal. Fines pass through and collect in liquid product.

The gas product from pyrolysis usually has a GCV of 15 -22 MJ/m^3 or a NCV of around 4-8 MJ/m^3 depending on feed and processing parameters [5].

2.6.1. Pyrolysis reactors

2.6.1.1. Fixed bed reactor

Char can be produced with a fixed bed reactor in which the biomass feedstock is partially gasified by pyrolysis environment. Products of this process are gas, viscous tars and charcoal of which the yield is maximized.

2.6.1.2. Fluidized bed reactor (FBR)

FBR technology offers good possibilities in gasifying biomass feedstocks with minimum tar formation. In that case, bed material should be selected on basis of optimum catalytic tar cracking behavior. If, however, tar is the product aimed at, a non-catalytic shallow fluid bed should be applied followed by immediate quenching of the gaseous products. Figure 2.9 is a fluidized bed reactor.

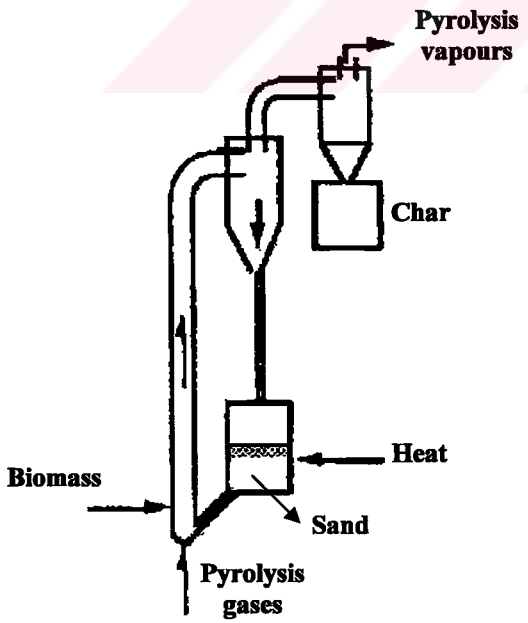

Figure 2.9: Fluidized bed reactor [30]

2.6.1.3. Entrained flow reactor

In the entrained flow reactor (Figure 2.10) propane is introduced stoichiometrically and pyrolysis occurs in the bottom section of the reactor. The produced hot flue gas flows upwards through the tube while passing the biomass. In this way the thermal energy of the gas is used to heat the biomass particles and, if necessary, provide the heat of the pyrolysis reaction.

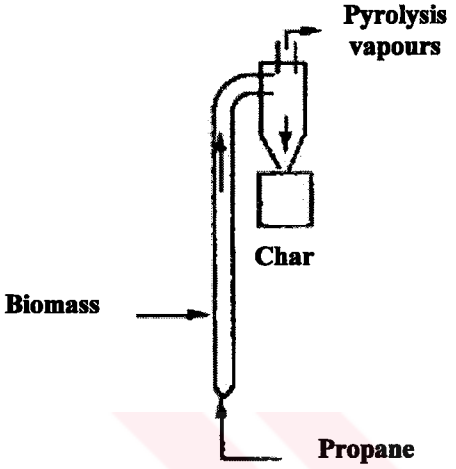

Figure 2.10: Entrained flow reactor [30]

2.6.1.4. Vacuum furnace reactor

Wood is fed into the top compartment of reactor and transported downwards by gravity and by the action of scrapers which at present in each compartment. If the biomedicine is converted completely, the bottom compartment contains only charcoal which can be easily removed from the reactor (Figure 2.11).

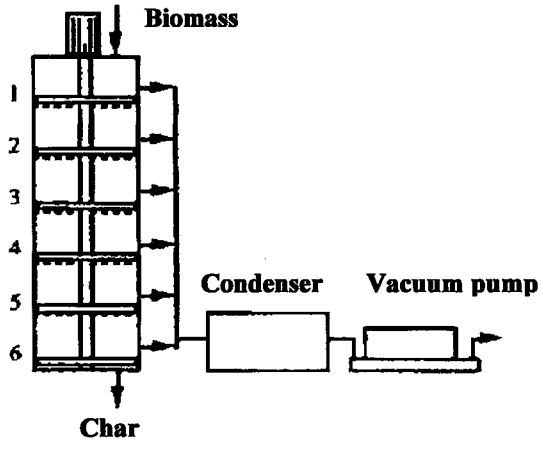

Figure 2.11: Vacuum furnace reactor [30]

2.6.1.5. Vortex reactor

For proper operation the reactor (Figure 2.12), biomass particles should be entrained in nitrogen flow with high velocity and enter the reactor tube tangentially. For such condition the biomass particles experience high centrifugal forces which induce high particle ablation rates on the heated reactor wall (890 K). The ablating particles leave a liquid film of bio-oil on the wall which evaporates rapidly. If the wood particles are not converted completely they may be recycled with a special solids recycle loop [30].

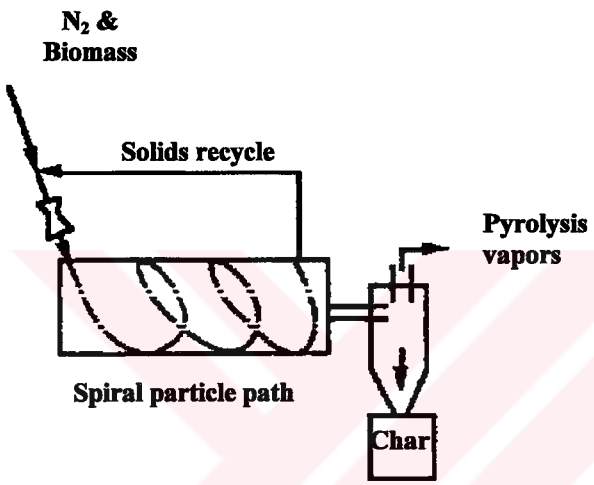

Figure 2.12: Vortex reactor [30]

3. COMBUSTION OF BIOMASS

Among all the processes and technologies to evaluate biomass as a fuel, combustion is the most dominant one. 95 % of the biomass energy used today is obtained with direct combustion.

Combustion systems are available for the conversion of virgin and waste biomasses into energy and also co-combustion systems are used to burn biomass together with fossil fuels [3].

3.1. Principles of Combustion

Ignition of biomass starts at high temperatures (at least 773 K) so the problem is to start it. Once ignition starts, if sufficient air is supplied, combustion will proceed. In that case, it is difficult to stop combustion before all the fuel present combusts.

The following stages can be distinguished in the combustion process:

Drying: Evaporation of the contained water

Volatile evolution and reduction: Thermal decomposition of fuel into volatile gases and solid char

Combustion of volatile gases above the fuel bed: Decomposition and reduction gases burn with yellow flames

Combustion of char: The solid char is combusted on the grate with blue flames or it glows.

Combustor systems, as seen in Figure 3.1, are composed of a furnace where the fuel is burned and a heat exchanger where the energy of the flue gas is transferred to a carrier media like water, steam or air.

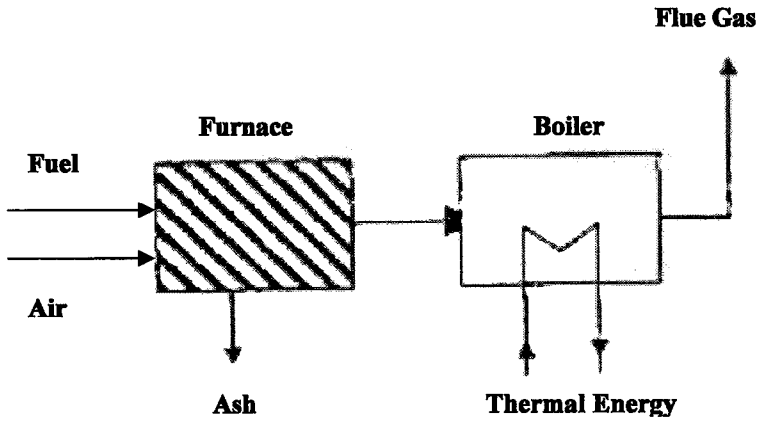

Figure 3.1: Basic process flow for biomass combustion [2]

The combustion process takes place in the furnace where the chemically bound energy is converted into thermal energy. The energy generated, excluding the losses to the environment (through furnace walls and hot ash) are transferred to the flue gas.

The efficiency of the furnace is expressed as in Equation 3.1:

$$\eta = \frac{\text{thermal energy available in the flue gas}}{\text{chemical energy in the supplied fuel}} \quad (3.1)$$

Where:

η = Efficiency of the furnace

Typical combustion efficiencies range from 65 % to 99 % [12].

Complete combustion (incineration, direct firing, burning) of biomass occurs due to the following oxidation reaction [3]:

$$(C_6H_{10}O_5)_n + 6n\ O_2 \rightarrow 6n\ CO_2 + 5n\ H_2O + \text{radiant and thermal energy} \quad (3.2)$$

cellulose

Combustion reactions are [5]:

$$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g) \quad (3.3)$$

$$H_2\ (g) + 1/2\ O_2\ (g) \rightarrow H_2O\ (l) \quad (3.4)$$

$$CH_4\,(g) + 2O_2 \rightarrow CO_2\,(g) + 2H_2O\,(l) \qquad (3.5)$$

The combustion of biomass is a stepwise process. The heat in the combustion chamber first dries the fresh biomass entering the chamber. The physical water and the non-combustible CO_2 in the biomass are evaporated. At 423-473 K, decomposition and devolatilization of solid biomass begins on the biomass surface and volatile organics are formed (evolution of combustible gases and tars). Above 553 K, the proportion of flammable gases emitted is high enough to burn. At this stage, combustion occurs with the presence of oxygen coming from air surrounding the combustion zone and at temperatures above the ignition temperature. The fuel content in the char residue burns with diffusion of oxygen to the surface at about 673-1073 K (release of chemically-bonded CO and chemically-formed H_2O) Once ignited, gases burn at a temperature of 1373 K. Char oxidation proceeds and continues until essentially all the carbon is oxidized. At higher temperatures, carbon oxides are the primary products. This temperature range is obtained with the energy of hot combustion gases and the radiant energy from the combustion chamber surface [2, 12, 18, 23].

When thermal degradation occurs in excess air, combustion occurs and heat is formed. With partial air, gasification occurs and products are fuel gases. With no air, pyrolysis occurs and products are mainly liquids and gases [5].

To provide complete combustion excess air is used for combustion. As air is the primary source of oxygen and 79 % of air is nitrogen, the most important emission in exhausts is nitrogen. The excess air factor lambda (λ) indicates the ratio between the real air supply and the theoretical amount of air needed for combustion. At stoichiometric combustion where $\lambda=1$, just sufficient air to burn all combustible particles is fed to the furnace [2]. It is important to remember that due to the diluting effect of air, the higher the excess air, the lower the temperature of the flue gas, which means energy losses in the system [2, 3]. Well-designed systems need less excess air [2].

The stoichiometric air demand of biomass is less than for coke and coals because biomass has a lower ratio of C/H. Besides; the carbon present in biomass is already partially oxidized. Less air is required for complete oxidation.

Combustion with the lack of excess air causes emissions of toxic, partially oxidized derivatives and particulate matter. Nitrogen and sulfur present in the biomass are oxidized and contributes to emissions. Also the nitrogen in combustion air is oxidized with the catalytic effect of high temperature with these reactions:

$$N_2 + O_2 \rightarrow 2NO \quad (3.6)$$

$$2NO + O_2 \rightarrow 2NO_2 \quad (3.7)$$

As temperature rises, the amount of NO formed increases. The quantity of chemically bonded nitrogen and sulfur in woody biomass is nearly zero. MSW contains relatively high amounts of elements like chlorine whereas woody biomass does not contain that. Existence of chlorine causes the formation of compounds like hydrogen chloride and these are accepted as hazardous. Emissions of CO, acidic gases, unburnt HC, partially oxidized organics, polycyclic aromatic derivatives, oxides of trace elements, oxides of nitrogen and sulfur, derivatives of chlorine, particulate carbon and fly-ash are formed in exhausts of not very well controlled combustor systems.

The ash content of the biomass does not change with combustion. It is evaluated as the difference between the original dry based weight and the weight of residual after combustion [3].

3.2. Combustion Systems (The Furnace)

The purposes of solid fuel combustor systems are to ratio and to mix the air fuel mixture, to start and to sustain ignition, to make the fuel volatile, to position the flame according to the heat release point and to enable all these provide the fuel in necessary amounts and pressure. The adequate hardware depends on fuel type, characteristics and amount; the final form required (heat, steam, electricity or cogeneration) the relation of the system with other systems of the plant (integrated, independent), the existence of recycling or co-combustion, methods to dispose wastes and environmental factors. The design parameters depend on the biomass composition (moisture, volatile matter, ash), specific heat of biomass, the drying and grinding equipment and emission levels.

The difference between conventional solid combustors and liquid or gas fuel combustors is that solid combustors have to allow more residence time for solids after the gases and liquids are separated. One way to speed up this process is to decrease fuel particle size beforehand [3].

Combustor systems are either fixed bed (manual-fed systems, spreader-stoker systems, under-screw systems, through-screw systems, cyclonic combustors, static grates and inclined grates) or fluidized bed systems (bubbling or circulating systems).

3.2.1. Fixed-bed systems

A fixed-grate system consists of a grate in a combustion room (forming the furnace). Primary air for combustion of the char is supplied under the grate and secondary air for combustion of the volatile gases is supplied above the grate. Combustion of the char provides heat for the decomposition of newly added fuel above the char. Typical combustion temperatures range from 1123 K to 1673 K. Ash is removed manually or automatically.

The high volatile content of biomass (compared to coal) requires larger combustion rooms.

In inclined grates, fuel is supplied at the top and moves downward during combustion. Ash is removed at the bottom.

In moving or sloping grates, the residence time of the pieces are fixed with the grate speed. Moving inclined grates are usually used for MSW burning systems. A sloping grate system is seen in Figure 3.2.

Screw feeders and spreader-stokers have been developed for smaller applications. Fuel particles are fed into the furnace above the reaction zone. Combustion takes place partly during the time that the particles move in suspension through the gas above the grate [2].

The stoker grate technology is effective in burning solid fuels that contain fuel particles of sufficient size that they must rest on a grate to burn as well as finely sized particles. Solid fuel is introduced into the furnace using pneumatic or mechanical spreaders which "stokes" (feeds) the furnace.

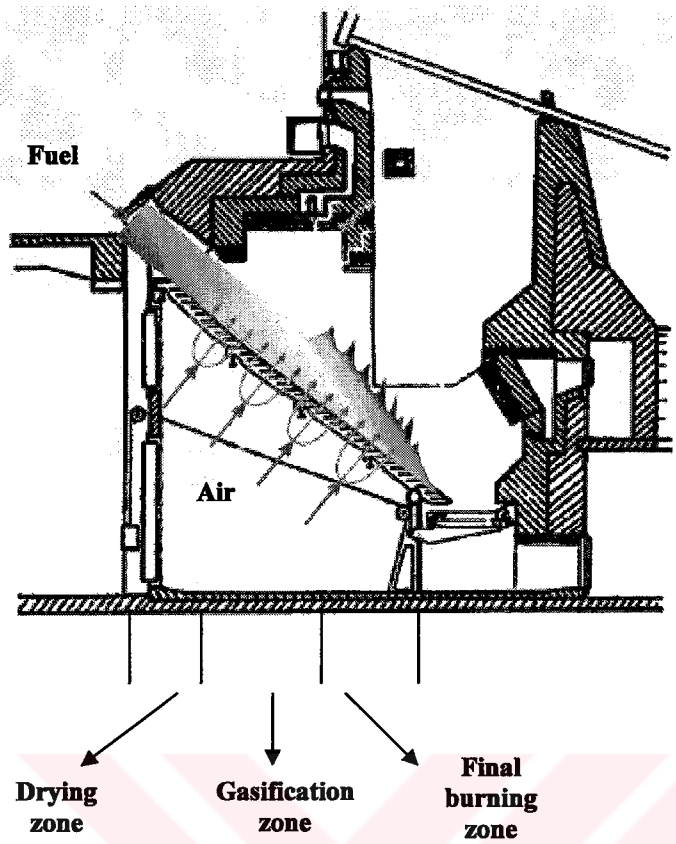

Figure 3.2: Sloping-grate combustion system [2]

If the stoker feeds fuel into the furnace by flinging it mechanically or pneumatically over the top of the grate, the stoker is referred to as a spreader stoker. The spreader stoker technology allows for the finely sized particles of the fuel to burn in suspension, while the larger solid fuel particles fall on the grate where they burn to completion. Spreader stokers with oscillating, pulsating, or travelling grates have been widely used for biomass power plants because many of the designed systems have the ability to burn a wide variety of solid fuels simultaneously. Furthermore, they respond more rapidly to load changes, and operate more efficiently with low excess air than crossfeed and underfeed units.

Typically, the spreader stoker feed system is more efficient than crossfeed and underfeed stoker systems [31]. Figure 3.3 shows a schematic of a spreader stoker furnace.

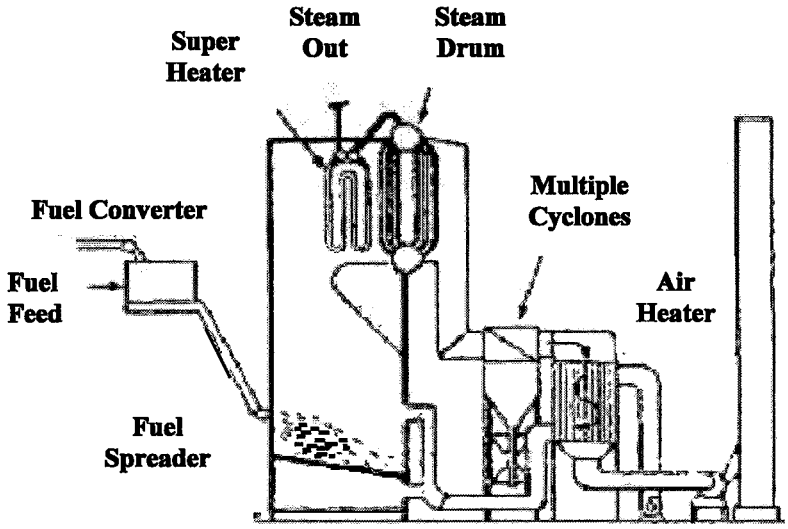

Figure 3.3: Spreader-stoker system with an integrated water-tube boiler [2]

In screw-feeder systems, the fuel is pushed up in the center of the combustion zone and ash is removed from the sides, manually or automatically. An underscrew feeder system is seen in Figure 3.4.

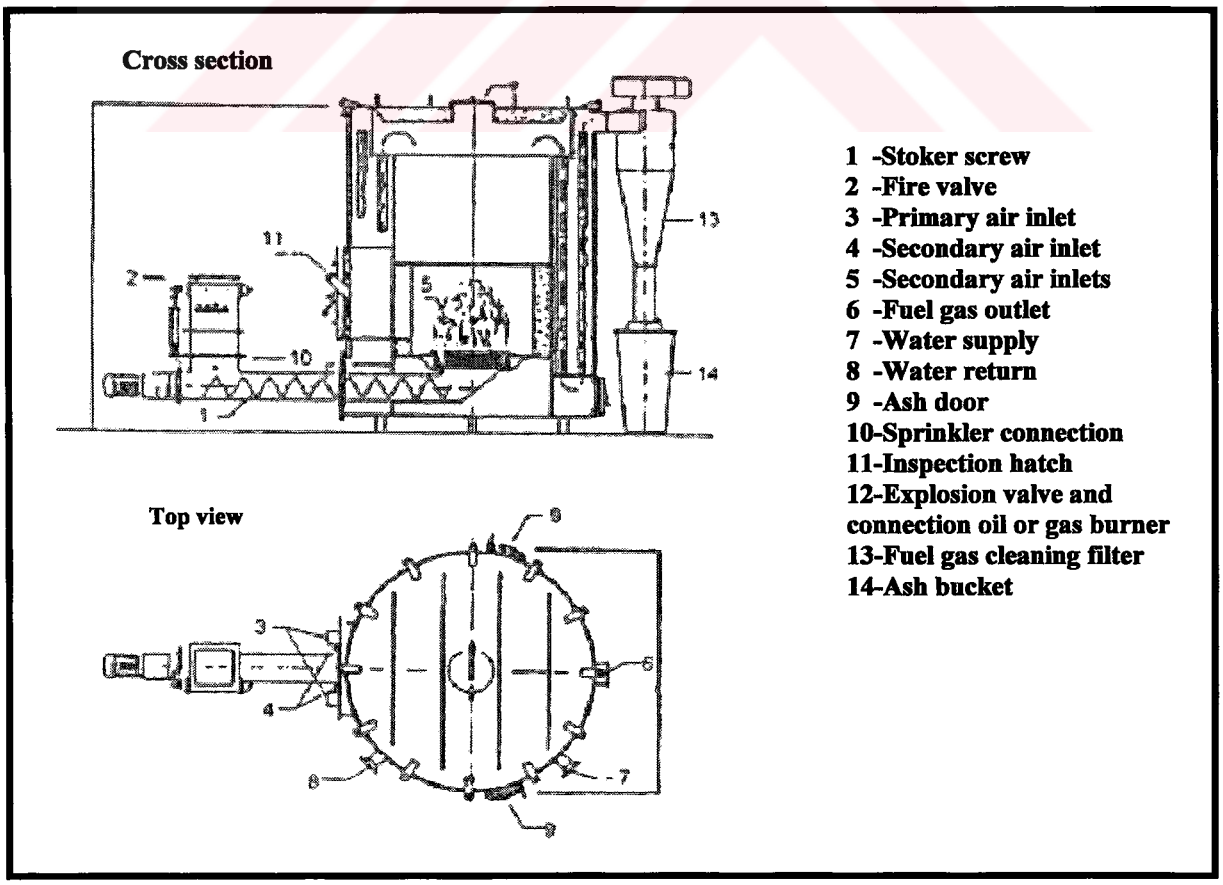

Figure 3.4: Combustion system with underscrew feeding system [2]

The through-screw system screw-feeds the fuel to the combustion zone while the fuel is burned. This type is more suitable for fuels with high ash content.

Cyclonic combustors (Figure 3.5) are suitable for burning waste wood and agricultural residues. Combustion air is introduced into a cylindrical chamber where cyclonic combustion air mixes the suspended particles allowing efficient combustion.

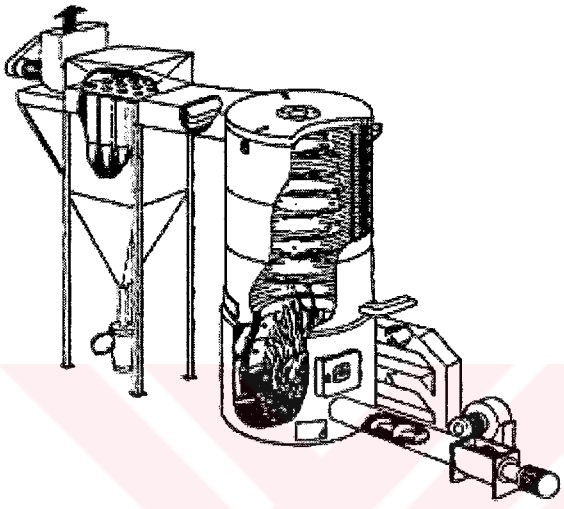

Figure 3.5: Cyclonic combustor [2]

3.2.2. Fluidized bed systems

In fluidized bed systems, the fuel is burned in a hot (973-1273 K) bed of sand, limestone or other material that is kept in turbulence by fans. Hot air or room temperature air is blown from the furnace bottom to the interior of the furnace to blow the fluid medium as if water boils. The sand bed acts as a heat-transfer medium and blowing air through a perforated bottom plate fluidizes the bed. Depending on the air velocity, the bed becomes bubbling or circulating [2, 32].

Waste is fed into this fluidized bed and burnt efficiently within a moment. Energy is saved by recovering the waste heat from furnace exhaust gas to heat combustion air and by recovering steam. As the odor components contained in exhaust gas is burnt and decomposed in the furnace, no deodorizing device is necessary. As the total amount of the incinerator ash is discharged with exhaust gas, it is required to collect particulates efficiently by using a filter dust collector, a cyclone or an electrostatic precipitator.

In bubbling type, the reactor has a zone containing freely moving sand particles by upward-streaming air and in the circulating bed type, air velocity is so high that bed and fuel particles flow upward with the gas stream and re-channeled into the reactor. During circulation light particles circulate and heavier particles burn until they are light enough to circulate [2]. Sewage sludge, municipal refuse, industrial waste, etc. can be combusted with fluidized beds [32].

Fluidized beds (Figure 3.6) offer the following advantages [2]:

- Flexibility to change fuel properties, sizes and shapes
- Acceptance of fuel moisture content up to 60 %.
- Acceptance of ash content up to 50 % .

Figure 3.6: Fluidized bed reactor [32]

The air is distributed uniformly into the bed via a perforated grid plate or a system of nozzles. To initiate combustion in the fluidized material, the bed temperature is elevated by using a startup fuel such as gas or oil, to a temperature capable of supporting combustion of the primary fuel.

In biomass units, during operation, biomass fuel and the inert bed material are continuously fed into the unit. The bed material becomes an isothermal reactor with heat transfer from the bed material to boiler tube surface and to the fresh fuel and air. The turbulent mixing of air and fuel at temperatures above the ignition point of the fuel causes combustion to take place without the need for conventional burners.

There are two major types of fluidized bed combustion (FBC) units. These are bubbling fluidized bed combustion (BFBC) and circulating fluidized bed combustion (CFBC). Each of these designs is suitable for operation either at atmospheric or pressurized conditions. Atmospheric FBC units are by far the most common and most commercially developed design. Furthermore, vendors offering both bubbling fluidized bed combustion (BFBC) and circulating fluidized bed combustion (CFBC) steam generators typically recommend BFBCs if the anticipated fuel is biomass alone. CFBCs are recommended if flexibility to burn both biomass fuels and coal is desired [31].

3.3. The Steam Cycle

With the thermal energy generated during combustion, electricity is generated using a steam cycle. The steam cycle composes of the furnace and boiler, the turbine, the condenser and the boiler feed-water pump. The cycle is as follows:

- The boiler feed water is pressurized by the pump and fed into the boiler
- Water is evaporated and superheated in the boiler
- The superheated steam is fed into a steam turbine where it expands to a low pressure and temperature that the condenser determines
- The expanded stream is fed from the condenser to the de-aerator
- Non-condensable gases dissolved in the feed water are removed

A steam cycle of a stoker grate boiler power generation plant is in Figure 3.7.

3.4. Factors Effecting Combustion

In the combustion of any fuel, there are three important factors, which include time, temperature, and turbulence [31].

It is becoming increasingly recognized that in order to understand biomass combustion and fully realize its potential benefits in the future energy mix; it is essential to gain a fundamental understanding of the relationship between fuel properties and combustion performance [7].

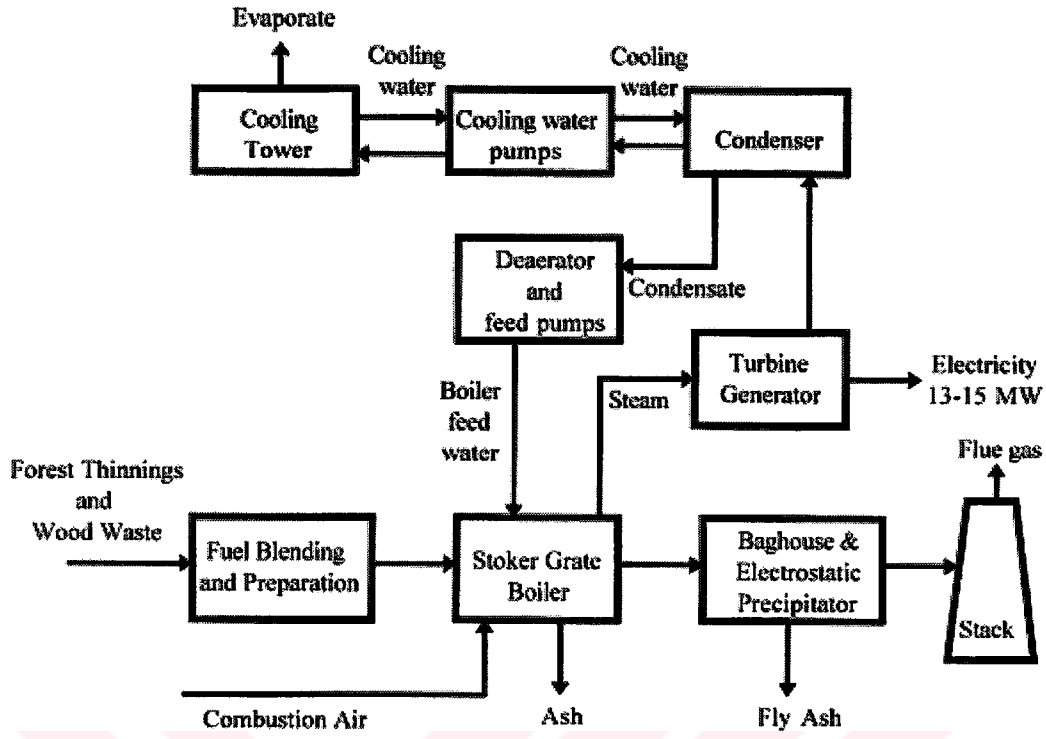

Figure 3.7: Steam cycle of a stoker grate boiler power generation facility [31]

Fuels in all categories combust in different manners due to environmental factors and composition properties. The thermal degradation characteristics of lignocelluloses are strongly influenced by their chemical composition (cellulose, hemicellulose and lignin contents) [6]. Volatile compounds like terpenes, which have a high energy content, combust with flames in gaseous phase. Solid lignins decompose with flames in gaseous phase forming pyrolysis products. The residual char burns slowly with surface oxidation and glowing. Cellulosic matter converts to combustible volatiles and non-combustible volatiles containing water and carbon dioxide whereas lignins contribute mostly to char formation [3].

Combustion efficiency depends on both the reduction of the unburnt components in the process and decreasing the emissions by the primary measures (the combustion process itself) and the secondary measures (emission reduction technologies) [8].

Some efficiency and environmental parameters are the extent of ash deposition (slagging and fouling), particulate emission levels, emissions of toxic trace inorganics and emission levels of greenhouse gases such as methane and nitrous

oxide. Many of the observed efficiency and environmental parameters are largely determined by the nature and extent of chemical reactions occurring among the many inorganic phases present in the firebox [7].

The size, shape and arrangement of fuel pieces affect the rate and completeness of combustion [12]. Smaller particles combust easily and completely whereas bigger particles require longer residence times [3].

Moisture is also an important value for biomass processes. If there is a high amount of moisture in the biomass, it is necessary to use more fuel to provide complete combustion. Moisture also decreases efficiency by causing low thermal efficiency, tar formation and too much emission. Biomasses with about 15-20 % moisture are preferred for conventional systems.

Combustion in small-scale hand-fired systems is a batch type process. In the early stages of combustion in such devices, in the volatile release phase, the formation of CO and HC, including PAH, is difficult to avoid. Some PAH compounds are very carcinogenic and CH_4 and other HC's contribute a net increase in the release of greenhouse gases.

Emissions from small-scale systems can be reduced by the use of catalytic converters. In certain stages of batch combustion, when the temperature is too low, the mixing of air and fuel can be non-homogenous and residence time can be too short for complete combustion. A catalytic converter will promote oxidation of unburnt flue gas components. Chemical reactions always choose the paths where the activation energy is lower and once the converter is ignited, it operates effectively at low temperatures [8].

3.5. Co-Firing

Co-firing is generally viewed as the most cost effective approach to biomass utilization by the electric utility industry. This process allows the consumption of fossil fuels to be reduced. The existing coal-fuelled power plants may be generally used with very little modifications.

Originally, co-firing was introduced as a means for utilities to accomplish the following objectives:

- Support economic development among wood products and agricultural industries in a given service area
- Reduce fossil CO_2 emissions as part of the voluntary global climate challenge program
- Reduce other airborne emissions including oxides of nitrogen (NO_x) and trace metals;
- Provide a means for transitioning to a broader base of biofuel supplies by developing infrastructural support for fuel supply and delivery.

Co-firing is a family of technologies. These include blending biomass with coal on the fuel pile, separately injecting biomass into a boiler, and gasifying biomass for subsequent firing in an electricity generating system [33].

Co-firing of biomass with natural gas is also an option. Natural gas is not used in this case as an alternative fuel but to achieve the following:

- Increase flame temperature to reduce emissions, stabilize combustion and reduce excess air
- Provide an independent, suspension-fired flame which improves load following (turndown capability) and reduces transients with fuel quality swings
- Reduce overall moisture when the fuel latent heat demand is causing incipient flameout [31].

A typical cofiring plant of 500 MW capacity has a conversion efficiency of 40 % compared with a 5 MW wood fired plant with 25 % efficiency.

There are four methods for co-firing:

- Firing pre-prepared wood through dedicated burners using separate wood forwarding systems
- Mixing pre-prepared wood and coal upstream of some or all of the burners and firing the mixture through those burners

- Pre-mixing wood chips with coal upstream of the existing coal preparation plant and co-preparing and firing of the fuel mixture through all of the burners
- Using an entirely separate wood fuelled boiler to raise steam to use in the main plant.

Potential benefits are low capital costs, high conversion efficiency and reduction of emissions of SO_2, CO_2 and NO_x [8].

One possible trade-off involves co-firing blends of coal and biomass in existing coal-fired power plants to retain the coal power infrastructure, but still making the most of the advantages of biomass. However, power-plant performance is closely related to the fuel composition and inherent differences between biomass and coal can affect three important factors:

- Efficiency – effected by moisture and volatile material content;
- Slagging and fouling – effected by properties of the ash;
- Erosion and corrosion – effected by chemistry of the emissions [14].

4. COMBUSTION KINETICS OF BIOMASS

Biomass has been used as an energy source since centuries and for more efficient and environmental usage of this fuel, new designs have been made in the configuration of combustion systems. Kinetic data is necessary for the design of processes by which productions of fuel gases, chemicals and energy, charcoal and activated carbon are carried out. Similarly, combustion kinetics of biomass should be well known for the development of combustion systems and furnaces. This kinetic data is usually obtained using thermogravimetric analyses.

The kinetics of thermal decomposition reactions of carbonaceous materials is complicated as the decomposition of these materials involves a large number of reactions in parallel and series. Although TGA provides general information on the overall reaction kinetics, rather than individual reactions, it could be used as a tool for providing comparison of the kinetic data which are under the effect of various reaction parameters such as temperature and heating rate [6].

4.1. Thermogravimetric Analysis (TGA)

Solid decomposition studies on a TG balance can be conducted both under isothermal and non-isothermal conditions. In pyrolysis studies the most common is constant heating rate TG is also known as "dynamic thermogravimetry". The results in this case are presented as a plot of weight loss vs. temperature or differential weight loss vs. temperature. Dynamic thermogravimetry has several advantages over the isothermal studies if one wishes to determine kinetic parameters:

- The kinetic parameters can be defined over the whole temperature range of the reaction.
- Continuous recording of weight loss with rising temperature assures that no features of the pyrolysis are overlooked.

- Less time is required to collect necessary data than would be required for isothermal analysis, since one dynamic experiment is equivalent to a large number of isothermal experiments.
- Only a single sample is required limiting any sample-to-sample error.

The analysis of these data is performed universally by making the assumption that the Arrhenius expression and its kinetic parameters, frequency factor and the activation energy are valid and that there are negligible barriers due to mass and heat transfer limitations.

Solid conversion function defines the dependence of rate of conversion on the concentration of reactant and product gases along with the rate of movement of reaction front within the solid. Several methods in differential and integral forms have been developed for the estimation of the kinetic parameters A, E and n where;

n= Reaction order [34].

Considerable attention is paid to the kinetic parameters calculation from TG curves. The present calculation methods are either based on a single TG curve or require several TG curves measured at various heating rates. Though a physical meaning of the kinetic parameters determined by single curve methods is not quite clear, these methods are able to describe a TG curve generally well. However, if a TG curve consists of two or more overlapping processes, the single curve methods usually fail.

It is possible to use iterative methods for the direct non-linear regression as a method of determining the kinetic parameters of heterogeneous reactions from TG curves [35].

A kinetic model for the combustion of biomass is proposed based on the hypothesis that each stage of weight loss stands for a reaction of one pseudo-part of the sample and that the kinetic parameters of each reaction keeps constant over the whole temperature range of the experiment. That means the number of weight loss stages equals the number of main reactions. In this model the evaporation of water and the residue of combustion are ruled out, and the conversion rate is adopted to indicate the reacting degree [17].

The chemical kinetics has in most cases been modeled according to one-step first order Arrhenius reaction. Disadvantages of such simple kinetics are that only total

volatiles are predicted and not how they are distributed among combustible and non-combustible gases, and the inability to account for the variation in char yield on dependence of operating conditions.

Another approach that has been used to model chemical kinetics is the so called lumped parameter approach where the reaction products have been grouped into classes of products such as gases, tars and char [8].

A simplified explanation of a TGA sample evaluation may be described as follows. A sample is placed into a TGA sample pan which is attached to a sensitive microbalance assembly. The sample holder portion of the TGA balance assembly is subsequently placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight (losses or gains) as heat is applied to the sample. TGA tests may be run in a heating mode at some controlled heating rate, or isothermally. Typical weight loss profiles are analyzed for the amount or percent of weight loss at any given temperature, the amount or percent of non-combusted residue at some final temperature, and the temperatures of various sample degradation processes.

TG analyzers are used to understand solid decomposition both qualitatively and quantitatively. They have also been used to determine kinetic parameters for various gas-solid reactions. In the case of solid fuels such as biomass and wastes it has mainly been used for the quantification of decomposition rates. It can also be used for the determination of some polymers and inorganic salts in a mixture.

4.2. Calculation of Kinetic Parameters from Thermogravimetric Data

Thermogravimetric analysis is one of the most extensive techniques to study the combustion kinetics of a fuel because of its simplicity and the information afforded by a single thermogram. Most kinetic studies use simple reaction models in different temperature range.

Some related definitions are given below:

Thermogravimetry (TG) technique bases on the detection of the changes of the sample mass with the program-controlled temperature.

Differential Thermogravimetry (DTG) technique determines the rate of the changes of the sample mass with the program-controlled temperature.

Differential thermal analysis (DTA) determines the relative temperature difference between the sample and the referenced material with the program-controlled temperature [17].

Isothermal thermogravimetry is that the mass of the sample is recorded as a function of time at constant temperature.

Quasi-isothermal thermogravimetry is that the mass of the sample is recorded when it gets constant in each temperature interval while the temperature is being increased in series.

Dynamic thermogravimetry is that the mass of the sample is recorded while the temperature is linearly changing.

TGA data is useful for determining the decomposition temperatures and rates of solid materials. Reaction rate parameters such as activation energy (E) and frequency factor (A) can be determined from constant heating rate data using a simplified Arrhenius equation [36].

Some methods to evaluate the kinetic coefficients using the non-isothermal TG curves are as follows [37]:

- "Integral methods" where the change of mass with temperature is used
- "Differential methods" where the rate of the mass change is used
- "Difference differential methods" where the secondary differences in the rate of the mass change are considered
- Specific methods that could be applied to first rates
- Methods where non-linear heating rates are used

A summary of these methods is seen in Table 4.1.

These methods are based on the combined usage of these equations:

$$\frac{d\alpha}{dt} = k * f(\alpha) \qquad (4.1)$$

$$k = A^{*}e^{-(E/RT)} \quad (4.2)$$

$$T = T_o + b^{*}t \quad (4.3)$$

Table 4.1: Methods to evaluate non-isothermal kinetic parameters [37]

Method Type	Method Name	Year Published
Integral Methods	Van Krevelen	1951
	Kissinger	1956
	Doyle Method (edited by Zsako)	1962
	Horowitz-Metzger	1963
	Coats-Redfern	1965
	D Harwadkar Karkhanavala	1969
	Integral method with multiple heating rates	1976
	Integral method with single heating rate	1986
	Urbannovici-Segal	1989
Differential Methods	Freeman-Carrol	1958
	Differential method with multiple heating rates	1965
	Sharp-Wentworth	1969
	Vachuska-Voboril	1971
	Cheng-Fong	1977
	Differential method with single heating rate	1992
Special Methods	Newkirk	1960
	Rich	1964
	Ingraham-Marier	1964
	Catterjee	1965
	Flayn-Wall	1966
	Freidmann	1969
	Satava-Skavara	1969
	MacCallum-Tanner	1970
	Sestak-Bergren	1971
	Carrol-Manche	1972
	Sestak-Satava	1973
	Rich-Stivala	1978
	Fatu-Segal	1983
	Popescu-Segal	1983
	Romero et all.	1984

Where;

$f(\alpha)$ = Differential form of the kinetic model

k = Reaction rate constant (s^{-1})

A = Frequency factor (s^{-1})

E = Activation energy (kcal*mol^{-1} or kJ*mol^{-1})

R = Gas constant (kcal*mol^{-1}*K^{-1}or kJ*mol^{-1}*K^{-1})

b = Constant heating rate (K*s-1)

T_o = Initial temperature (K)

α = Conversion

T = Temperature at time t (K)

Conversion is evaluated with the following equation:

$$\alpha = \frac{(W_o - W_t)}{(W_o - W_\infty)} \tag{4.4}$$

W_o = Initial weight of the sample

W_t =Weight of the sample at time, t

W_∞ =Weight of the sample at the end of the reaction

When equations 4.1, 4.2 and 4.3 are combined:

$$\frac{(d\alpha / dT)}{f(\alpha)} = (A/b)*e^{-(E/RT)} \tag{4.5}$$

This equation is linearized taking the logarithm of both sides:

$$\ln \frac{(d\alpha /dT)}{f(\alpha)} = \ln [\frac{A}{b}] - [\frac{E}{R*T}] \tag{4.6}$$

In order to determine the kinetic constants, the linearized equation has been solved with many different f (α) assumptions. When the left side of the equation is sketched versus 1/T, the shift of the resulting line gives the ln [A/b] value and the slope gives [-E/R] value. f(α) is the most suitable function that represents the degradation reaction.

The most suitable method to determine the kinetic parameters of biomass using the TG curves is the Coats-Redfern method [38]. Assume the degradation reaction:

$$aA\ (s) \leftrightarrow bB\ (s) + cC\ (g) \tag{4.7}$$

This integral method expresses the disappearance rate of A with equation (4.7), assuming:

$$f(\alpha) = (1-\alpha)^n \tag{4.8}$$

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{4.9}$$

The integral of equation (4.9) is taken and linearized in order to find equations to evaluate kinetic variables. These are:

For n≠1;

$$\log\left[\frac{1-(1-\alpha)^{(1-n)}}{(1-n)T^2}\right] = \log\left[\frac{AR}{bE}\right]\left[\frac{1-2RT}{E}\right] - \left[\frac{E}{2.303RT}\right] \tag{4.10}$$

The appropriate n value is selected and the plot of 1/T versus $\log\left[\frac{1-(1-\alpha)^{(1-n)}}{(1-n)T^2}\right]$ is sketched and the slope of the resulting line gives E value and the shift gives A value.

For n=1;

$$\log\left[-\log\frac{(1-\alpha)}{T^2}\right] = \log\left[\frac{AR}{bE}\right]\left[\frac{1-2RT}{E}\right] - \left[\frac{E}{2.303RT}\right] \tag{4.11}$$

The plot of 1/T versus $\log\left[-\log\frac{(1-\alpha)}{T^2}\right]$ is sketched and the slope of the resulting line gives $\left[\frac{E}{2.303RT}\right]$ value and the shift gives $\log\left[\frac{AR}{bE}\right]$ value [38, 39].

Table 4.2 shows the possible models using different f(α) assumptions.

Some of the kinetic parameters available in the literature are listed in Appendix A.

Table 4.2: Models with different f(α) assumptions [37]

Equation	Definition	Differential Form f(α)	Integral Form $g(\alpha) = \int d(\alpha)/f(\alpha)$
1. First Order (n=1)	Chemical Kinetics (Fn 1)	$(1-\alpha)$	$[-\ln(1-\alpha)]$
2. Zero Order (n=0)	Chemical Kinetics (Fn 0)	1	α
3. 1/3. Order (n=1/3)	Chemical Kinetics (Fn 1/3)	$(1-\alpha)^{1/3}$	$(3/2).[1-(1-\alpha)^{2/3}]$
4. 1/2. Order (n=1/2)	Chemical Kinetics (Fn 1/2)	$(1-\alpha)^{1/2}$	$2.[1-(1-\alpha)^{1/2}]$
5. 2/3. Order (n=2/3)	Chemical Kinetics (Fn 2/3)	$(1-\alpha)^{2/3}$	$3.[1-(1-\alpha)^{1/3}]$
6. Second Order (n=2)	Chemical Kinetics (Fn 2)	$(1-\alpha)^{2}$	$[1.(1-\alpha)^{-1}]$
7. Third Order (n=3)	Chemical Kinetics (Fn 3)	$(0,5).(1-\alpha)^{3}$	$[1.(1-\alpha)^{-1}]^2$
8. Phase boundary controlled rxn.	Interaction geometry in cylindrical symmetry (R2)	$2.(1-\alpha)^{1/2}$	$1-(1-\alpha)^{-1/2}$
9. Phase boundary controlled rxn.	Interaction geometry in cylindrical symmetry (R3)	$3.(1-\alpha)^{2/3}$	$1-(1-\alpha)^{-1/3}$
10. Avrami-Erofeev (n=1.5)	Random nucleation and growth of core (A1.5)	$(1,5).(1-\alpha).[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
11. Avrami-Erofeev (n=2)	Random nucleation and growth of core (A2)	$2.(1-\alpha).[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
12. Avrami-Erofeev (n=3)	Random nucleation and growth of core (A3)	$3.(1-\alpha).[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
13. Avrami-Erofeev (n=4)	Random nucleation and growth of core (A4)	$4.(1-\alpha).[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
14. Valensi Barrer	2-D diffusion (D2)	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1+\alpha).\ln(1-\alpha)$
15. Jander	3-D Diffusion in spherical symmetry (D3)	$(3/2).(1-\alpha)^{2/3}.[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
16. Ginstling Brounstain	3-D Diffusion in cylindrical symmetry (D4)	$(3/2).[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(2/3).\alpha]-(1-\alpha)^{2/3}$
17. Prout-Tompkins	Branching Core (B1)	$\alpha.(1-\alpha)$	$\ln[\alpha.(1-\alpha)^{-1}]$
18. Prout-Tompkins	Branching Core (B2)	$0,5.(1-\alpha).[-\ln(1-\alpha)]^{-1}$	$[-\ln(1-\alpha)]^2$
19. Prout-Tompkins	Branching Core (B3)	$(1/3).(1-\alpha).[-\ln(1-\alpha)]^{-2}$	$[-\ln(1-\alpha)]^3$
20. Prout-Tompkins	Branching Core (B4)	$(1/4).(1-\alpha).[-\ln(1-\alpha)]^{-3}$	$[-\ln(1-\alpha)]^4$

5- EXPERIMENTAL

5.1. Thermogravimetric Analyzer

The thermogravimetric system (Shimadzu TG 41) was used in decomposition experiments. Maximum operating temperature of the device is 1773 K and the thermocouple used is a Pt-Rh alloy. The cylindrical aluminum sample holder has a 10 mm diameter and 14 mm height. The cross-section of the device is shown schematically in Figure 5.1.

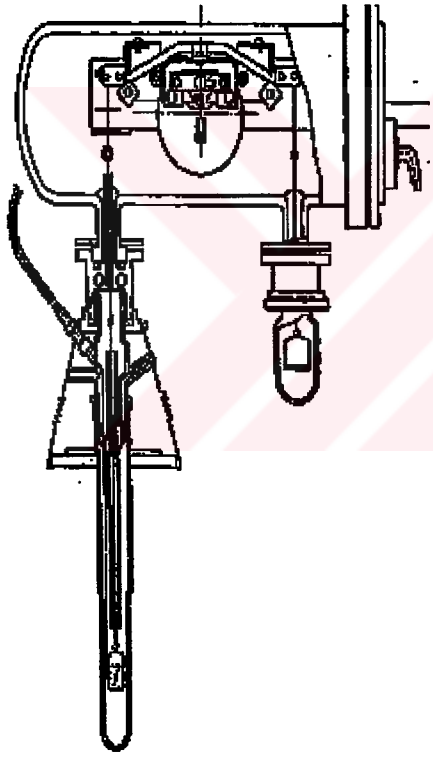

Figure 5.1: Cross section of TG analyzer

5.2. Selection of the Samples

The samples used in this study are widely available in Turkey. Production amounts and residual amounts are tabulated in Table 5.1 [40, 41, 42].

Table 5.1. Production and residual amounts of samples [40]

Sample	Productions (tons)	Total Actual Residues (tons)
Olive Residue	1.631.988	853.738
Sunflower	2.839.006	2.349.387
Rapeseed	6.500	-
Walnut Shell	144.008	107.857
Tea	145.000	-
Cotton	990.000	-
Grape	3.500.000	-
Sour Cherry Stone	114.466	39.916

5.3. Experimental Conditions

Thermogravimetric analyses of olive bagasse, sunflower shell seed, rapeseed, walnut shell, pinecone, tea residue, cotton bagasse, grape seed, hybrid poplar, and sour cherry stone have been carried out.

For all TG experiments, the recording paper speed is chosen as 2.5 mm/min. 40 mg of samples with particle size <250 μm are burned.

Air with 40 cc/min flow rate was used as the oxygen source. Samples have been heated up to 378 K with 10 K/min heating rate and were held at that temperature until the mass loss rate is zero (10 min). Then with heating rates of 5 K/min and 10 K/min, samples have been heated up to 1173 K and held at that temperature until mass loss rate is zero (30 min).

The TG curves obtained and the DTG curves derived are given in Appendix B.

5.4. Analyses of the Samples

Detailed information about the biomass types used in this study are available in the literature [1].

Moisture, volatile matter, fixed carbon, and ash contents of the biomass samples were determined according to ASTM standards. Gross and net calorific values were determined by bomb calorimeter method. Percentages of C,H,O, and N present in the biomass were found using EuroEA3000 model elemental analyzer. Structural compositions of the biomass samples were carried out by analytical means to determine the extractives, lignin, holocellulose, and α-cellulose contents.

The results of the proximate analyses on original-base are given in Table 5.2.

Table 5.2: Proximate analyses on original-base, % [1]

Sample	Moisture	Volatile Matter	Fixed Carbon	Ash
Olive bagasse	11,50	62,75	9,50	16,25
Sunflower shell seed	10,25	76,00	10,00	3,75
Rapeseed	14,25	77,00	5,00	3,75
Walnut shell	10,00	73,50	15,25	1,25
Pine cone	12,50	70,75	15,50	1,25
Tea residue	10,37	73,38	15,00	1,25
Cotton bagasse	8,75	76,75	10,75	3,75
Grapeseed	10,50	70,00	15,00	4,50
Hybrid poplar	10,00	77,50	11,25	1,25
Sour cherry stone	7,60	75,89	14,01	2,50

The proximate analyses results indicate that the range of moisture, volatile matter, fixed carbon and ash contents of the biomass samples vary between 7,60-14.25 %, 62.75-77.50 %, 5,00-15.50 % and 1.25-16.25 %, respectively.

The results of the calorific analyses are given in Table 5.3.

Table 5.3: Calorific analyses results, as received [1]

Sample	GCV (MJ/kg)	NCV (MJ/kg)
Olive bagasse	14,85	15,94
Sunflower shell seed	16,03	17,60
Rapeseed	14,82	16,40
Walnut shell	17,02	18,31
Pine cone	16,83	18,38
Tea residue	20,82	22,82
Cotton bagasse	16,06	17,58
Grapeseed	18,82	20,51
Hybrid poplar	15,60	17,14
Sour cherry stone	20,08	21,32

When the GCV's of the samples are compared, it is observed that tea residue has the highest GCV while olive bagasse has the lowest.

The results of the ultimate analyses on dry-base are given in Table 5.4.

Table 5.4: Ultimate analyses on dry-base, % [1]

Sample	C	H	N	O
Olive bagasse	39,00	4,00	1,00	34,96
Sunflower shell seed	50,00	6,00	-	40,38
Rapeseed	41,00	6,00	5,00	39,87
Walnut shell	36,38	4,73	-	55,00
Pine cone	44,00	6,00	-	43,11
Tea residue	39,29	8,46	2,93	42,96
Cotton bagasse	42,00	6,00	3,00	44,23
Grapeseed	41,97	6,58	2,12	44,05
Hybrid poplar	43,00	6,00	-	47,56
Sour cherry stone	38,13	5,08	0,16	52,02

According to Table 5.4, sunflower shell seed has the highest C content where walnut shell has the lowest. Tea residue is the richest in H content where olive bagasse has the lowest H ratio. The N contents of sunflower shell seed, walnut shell, pine cone and hybrid poplar could not be determined as they were below the lower limit of the measuring device. Rapeseed, on the contrary, has a very high N content. Walnut shell has a high percentage of O and olive bagasse has the lowest O content.

The results of the structural analyses on a dry-base are given in Table 5.5.

Table 5.5: Structural analyses on dry base, % [1]

Sample	Extractive Matter	Lignin	Holocellulose	α-Celulose
Olive bagasse	12,48	31,71	36,56	14,90
Sunflower shell	12,40	28,22	56,13	25,57
Rapeseed	14,31	27,74	50,30	13,63
Walnut shell	8,26	42,47	45,77	24,31
Pine cone	9,90	37,35	46,50	18,81
Tea residue	20,56	18,74	54,67	29,67
Cotton bagasse	16,28	17,57	61,77	40,26
Grapeseed	17,81	37,48	39,96	17,90
Hybrid poplar	4,07	26,28	66,53	49,14
Sour cherry stone	19,34	24,66	51,62	19,92

The extractive matter contents of the sample vary between 4.02-21.15 % and the lignin contents vary between 17.57-49.77 %. Cotton bagasse has the highest holocellulose whereas olive bagasse has the lowest. Hybrid poplar has the highest α-cellulose where rapeseed has the lowest.

6- RESULTS AND DISCUSSION

Some important parameters that predict the burning behavior of the samples under investigated conditions are maximum burning rate and the corresponding temperature determined from the intensity, the temperature of the highest peak on the DTG curves, and the burning time which is described as the overall time required for the completion of the mass loss from the biomass samples. These data are tabulated in Appendix C.

The direct relationships between these data for both heating rates have been compared with structural composition, ultimate, calorific analyses and proximal analysis results. Some meaningful relationships were observed. The resulting trends are explained in the figures below.

In Figure 6.1, it can be seen that increasing extractive matter content of the biomass samples leads to increase in the burning times during the process. Extractives as well as lignin are thermally less reactive than holocelluloses and consequently, increasing extractive matter content of the biomass samples led to longer burning times. On the other hand, extractive matter may contain some mineral species which are extractable under the test conditions, and these species may play inhibiting role on combustion under studied process conditions [43].

Ash is a transformed remnant of the mineral species in any fuel material as a result of thermal disintegration during combustion. Since mineral species are not combustible, they have no direct contribution to combustion. However, it is well known that some of these species have important catalytic effects on the combustion process [44, 45]. During the combustion of the biomass samples with less ash, higher maximum burning rate values were determined due to the fact that no diluting effects of the inorganics were present and, consequently these samples become relatively rich in combustible organic part (Figure 6.2). In literature, it is reported that lower burning rate of high ash content fuel resulted in char particles left without being fully burnt.

The combustion behavior of high ash coals was also investigated and it has been found that the burning rate was reduced by a factor of 4-5 in the case of high ash [46].

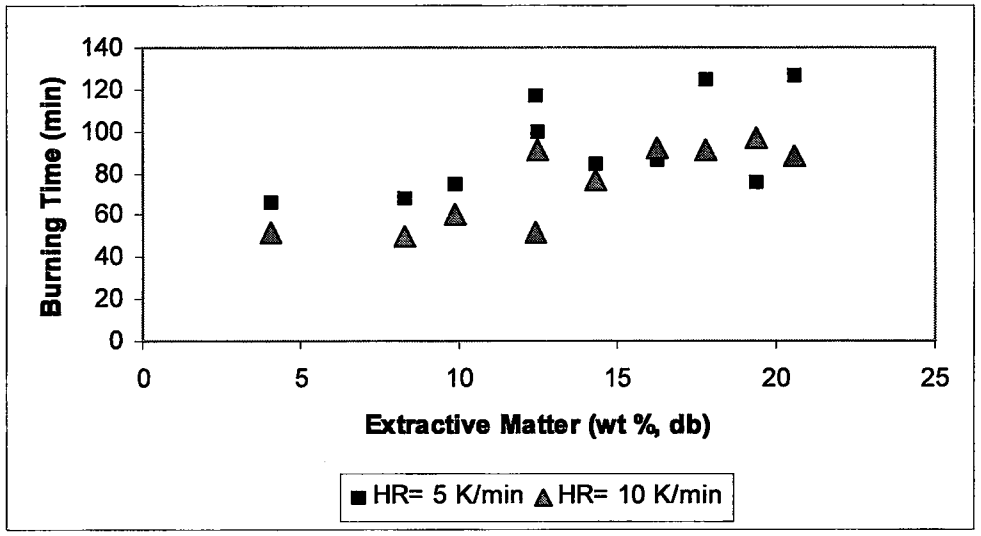

Figure 6.1: Extractive matter content vs. burning times

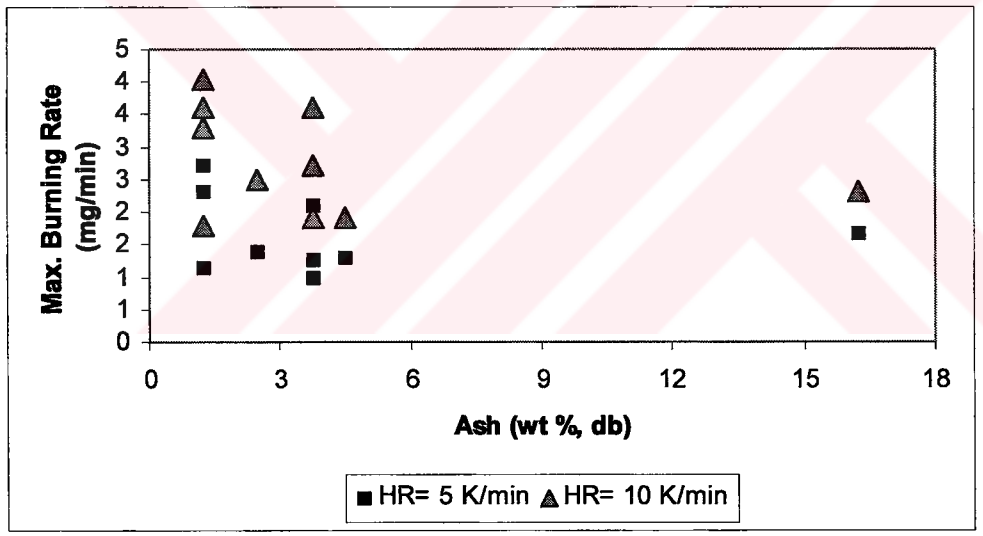

Figure 6.2: Ash content vs. max. burning rate

Figure 6.3 summarizes the effects of the burning time on the maximum burning rates of the samples. Although the value of the maximum burning rate represents only one point in the range of the burning rates at the investigated temperature interval, the general trend is that the biomass samples which have high values of maximum burning rates also have high overall burning rates and the times required for complete burning of these samples are shorter. In case of longer burning times, lower maximum burning rates were observed in general. This shows that the burning of these samples takes place relatively at lower rates and from this point of the view their burning can

be considered as more stable, and they necessitate longer times for completion of the burning process.

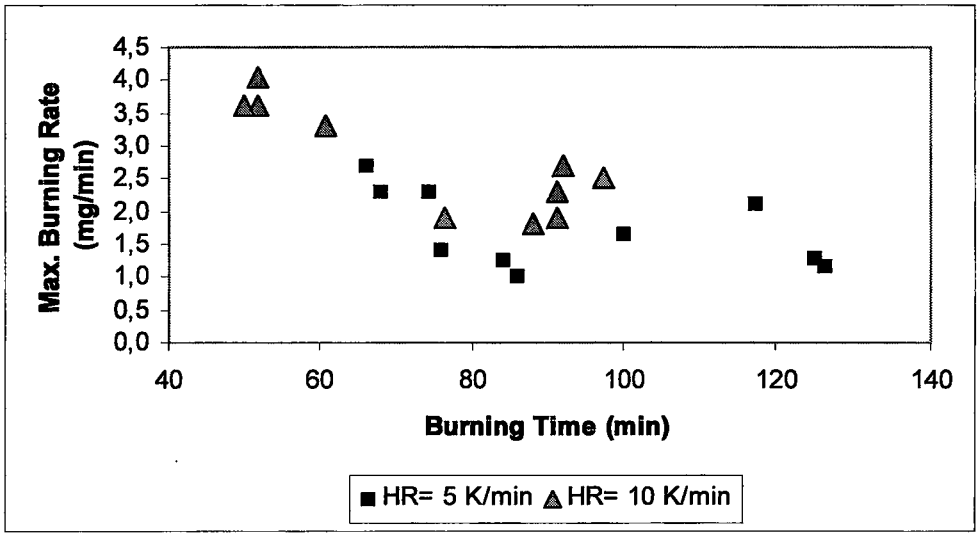

Figure 6.3: Burning time vs. max. burning rate

The major biomass constituents such as hemicellulosics and cellulosics give the most important contribution to the intensity of the main burning peak on the DTG curves. These constituents are not in the group of the extractive matter. Thus, if a biomass sample contains relatively lower extractive matter, hemicellulosics and cellulosics may be more concentrated, and consequently some increase can be observed on the maximum burning rate (Figure 6.4).

Although Figure 6.5 shows a scattered trend of the data, it can be concluded that biomass samples with relatively higher gross calorific value have higher temperatures at which maximum burning rates are recorded. Almost all of the calorific value of a biomass sample is resulted from holocellulose (hemicellulose + cellulose), lignin, and extractives. Higher temperatures of maximum burning rate for the samples that have relatively higher gross calorific value can be attributed to effects of these constituents.

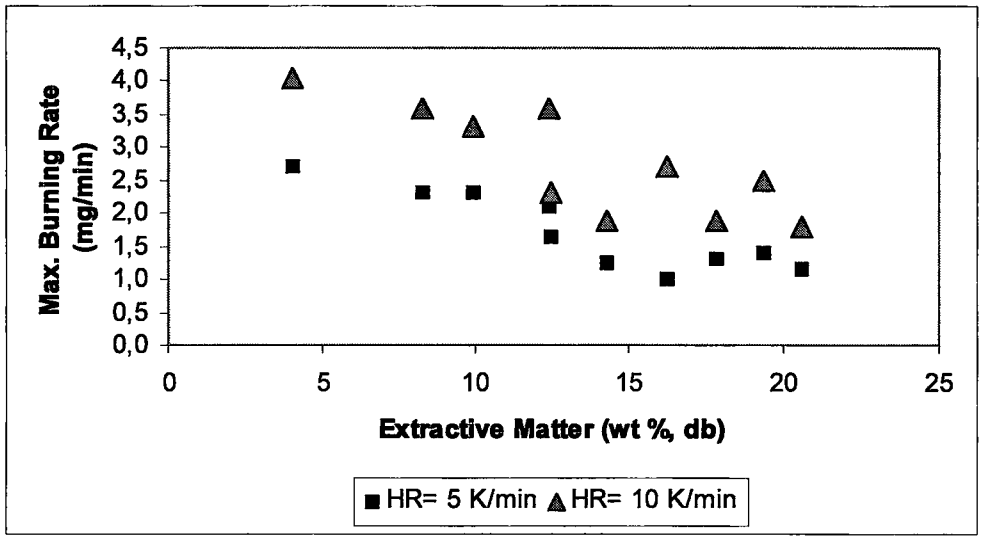

Figure 6.4: Extractive matter content vs. max. burning rate

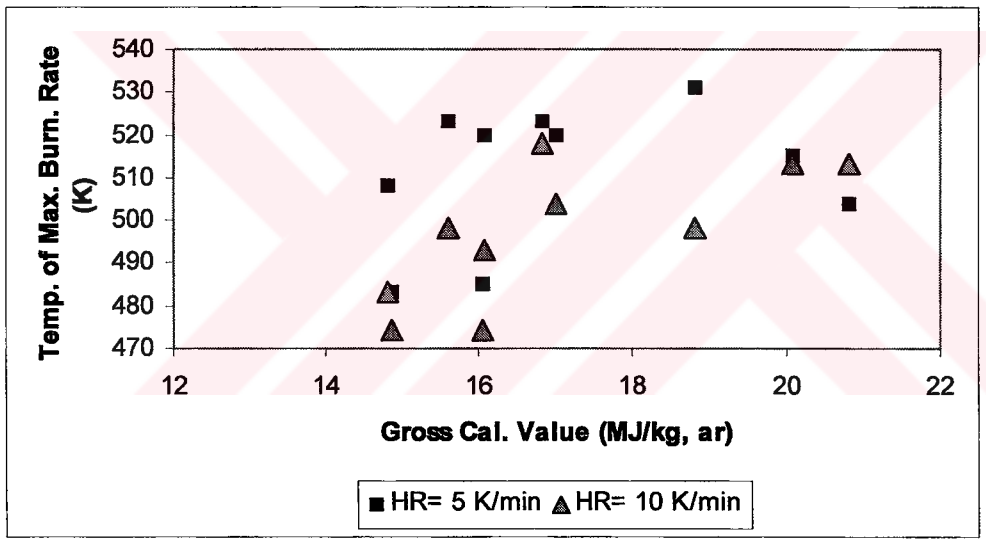

Figure 6.5 : Gross calorific value vs. temperature of max. burning rate

In Figure 6.6, the relation between the volatile matter content of the biomass samples and the maximum burning rate is given. It is well known that the thermal disintegration of the cellulosic materials begins by hemicellulose decomposition and after that cellulose decomposition takes place upon heating. Volatiles from these decompositions contain some combustible and non-combustible species. Non-combustible species leave the medium as they are, whereas combustible species undergo combustion if the temperature is high enough. Maximum burning rates on the DTG curves for typical biomass samples are generally recorded during decomposition of the cellulosic compounds. Therefore, biomass samples having relatively higher volatile matter contents are seen to have higher maximum burning rates. On the other

hand, increasing volatile matter content of a fuel was reported to lower the ignition point of the fuel [47].

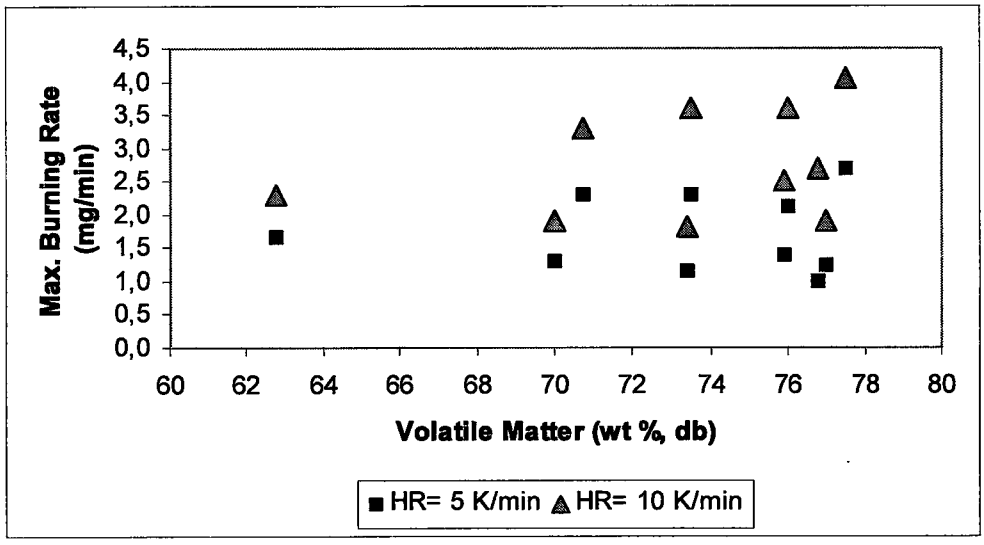

Figure 6.6: Volatile matter content vs. max. burning rate

Figure 6.7 presents the relation between the fixed carbon content of the biomass samples and the maximum burning rate. As fixed carbon content increases, a slight increase in maximum burning rate is observed.

Some volatile species forming from biomass at lower temperatures, which are either non-combustible or temperature is too low for their combustible ingredients, have no contribution to the calorific value measured, and besides the maximum rates of mass losses from the biomass samples are commonly resulted from these volatile evolution process. On the other hand, lignin content of biomass has a slower but more steadily burning characteristics. For this reason, biomass samples with relatively lower gross calorific value are seen to have higher maximum burning rates compared with those having higher gross calorific values. This relation is given in Figure 6.8.

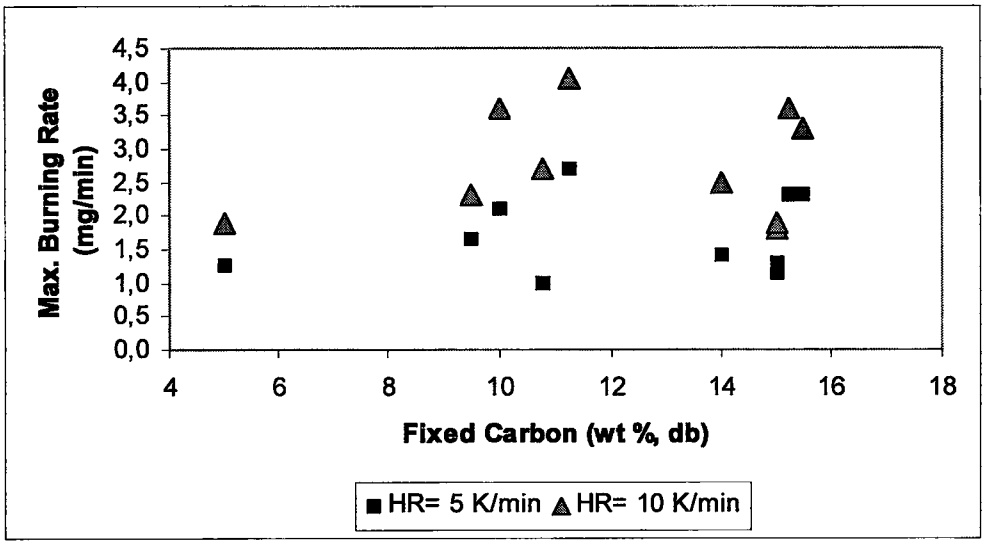

Figure 6.7: Fixed carbon content vs. max. burning rate

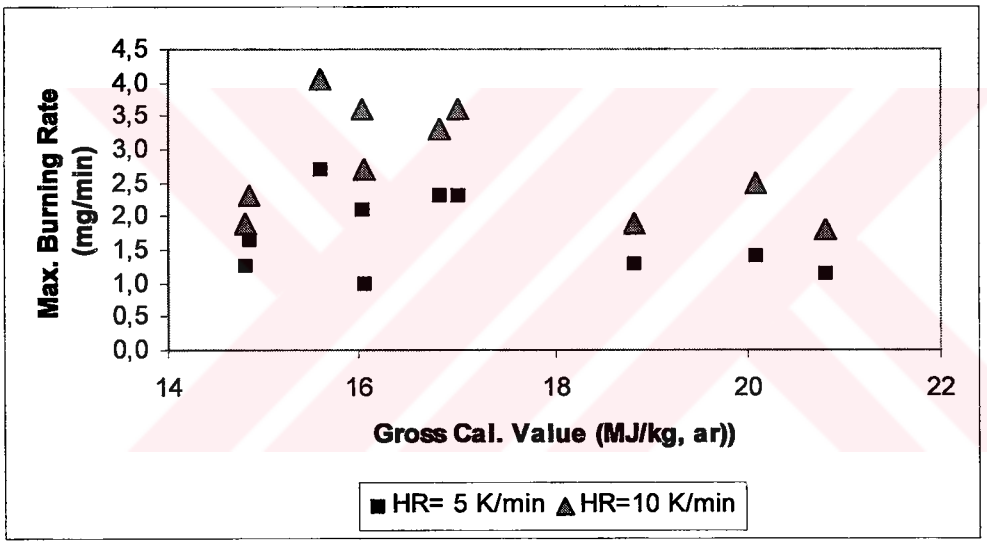

Figure 6.8: Gross calorific value vs. max. burning rate

For all samples, kinetic parameters have been evaluated under dry air atmosphere with heating rates of 5 K/min and 10 K/min, separately. The overall kinetic parameters and kinetic model (of the whole temperature range) and the parameters within every interval of 100 K have been separately investigated. E and log A values and the kinetic model are tabulated in Table 6.1 and the definition of the kinetic models were listed in Table 4.2.

Table 6.1: Kinetic parameters

Sample	Heating Rate (K/min)	T range (K)	R^2	E (kJ/mol)	log A	Model	$t_{combustion}$ (min)
Olive waste	5	overall	0,98703	46,79	4,067	Fn2	68,00
		378-673	0,98703	46,79	4,067	Fn2	
		673-722	0,92377	16,68	2,535	D3	
	10	overall	0,91916	27,04	3,090	Fn2	64,00
		378-673	0,93450	10,30	2,402	Fn3	
		673-773	0,98957	37,43	3,357	B4	
		773-873	0,99235	45,24	3,849	B4	
		873-978	0,94655	54,46	4,262	B4	
Sunflower seed shell	5	overall	0,92667	39,98	3,613	Fn2	88,00
		378-673	0,94703	17,81	2,723	Fn3	
		673-773	0,99409	10,52	1,306	D4	
		773-818	0,99201	11,41	1,733	D4	
	10	overall	0,97195	40,52	3,871	Fn2	52,00
		378-673	0,94893	17,34	2,990	Fn3	
		673-773	0,98973	49,22	4,304	B4	
		773-903	0,94831	21,16	2,650	B1	
Rapeseed	5	overall	0,92341	51,79	4,144	B4	84,00
		378-673	0,95557	41,78	3,702	Fn3	
		673-773	0,99330	16,19	1,926	D2	
	10	overall	0,85210	86,01	5,155	B4	76,40
		378-673	0,94465	9,80	2,347	Fn3	
		673-773	0,95192	15,43	2,349	B4	
		773-873	0,87229	16,91	2,466	B4	
		873-973	0,80202	22,27	2,718	B4	
Walnut shell	5	382-723	0,98517	59,07	4,591	Fn2	68,00
	10	overall	0,95450	51,71	4,379	Fn2	50,00
		380-673	0,96189	59,59	4,839	Fn2	
		673-883	0,96850	25,18	2,490	D3	
Pine conifer	5	overall	0,97843	59,22	4,529	Fn2	74,40
		378-673	0,98330	56,04	4,380	Fn2	
		673-748	0,99522	19,23	2,144	D2	
	10	overall	0,93796	46,83	4,057	Fn2	60,80
		378-673	0,95591	59,64	4,780	Fn2	
		673-773	0,99002	52,56	4,266	B4	
		773-873	0,99143	77,71	5,153	B4	
		873-973	0,98480	15,32	1,810	D4	

Sample	Heating Rate (K/min)	T range (K)	R^2	E (kJ/mol)	log A	Model	$t_{combustion}$ (min)
Tea residue	5	overall	0,93536	68,60	4,268	D4	108,40
		378-673	0,93536	68,60	4,268	D4	
		673-773	0,99592	59,38	4,182	B4	
		773-873	0,90225	22,51	2,346	B4	
		873-973	0,98549	33,24	2,317	D4	
	10	overall	0,92792	95,63	5,636	B4	64,00
		378-673	0,92656	43,73	4,103	Fn2	
		673-773	0,64983	55,51	4,484	Fn3	
		773-873	0,99311	44,31	3,721	B4	
		873-1021	0,95773	17,99	2,110	D2	
Cotton residue	5	overall	0,95479	162,20	8,390	B4	86,00
		378-673	0,96479	47,95	3,954	Fn2	
		673-773	0,99783	36,58	2,713	D3	
		773-813	0,98714	101,48	5,059	D3	
	10	overall	0,90200	108,94	6,166	B4	68,00
		375-673	0,93693	43,97	4,064	Fn2	
		673-773	0,99781	41,22	3,680	B3	
		773-873	0,99781	48,79	3,970	B4	
		873-973	0,97075	69,51	4,680	B4	
Grapeseed	5	overall	0,96046	135,78	7,170	B4	96,80
		378-673	0,97279	41,57	3,604	Fn2	
		673-773	0,99790	23,26	2,431	B1	
		773-873	0,99533	15,79	1,833	D2	
	10	overall	0,93828	117,16	6,360	B4	68,00
		378-673	0,95901	44,45	4,025	Fn2	
		673-773	0,99707	38,63	3,505	B4	
		773-873	0,99430	57,97	4,245	B4	
		873-1013	0,98250	12,06	1,553	D4	
Hybrid poplar	5	overall	0,98141	66,81	4,960	Fn2	66,00
	10	overall	0,93368	41,69	3,911	Fn2	52,00
		378-673	0,95910	64,40	4,960	Fn2	
		673-773	0,99534	53,43	4,440	B4	
		773-903	0,91262	11,73	1,640	D4	
Sour cherry stone	5	overall	0,96797	42,61	3,711	Fn2	76,00
		378-673	0,97143	44,95	3,854	Fn2	
		673-773	0,99277	12,42	1,676	D2	
	10	overall	0,92135	29,18	3,163	Fn2	70,00
		378-673	0,95719	46,51	4,180	Fn2	
		673-773	0,99403	33,12	3,360	B4	
		773-873	0,97352	35,69	3,450	B4	
		873-973	0,99140	65,25	4,490	B4	
		973-1058	0,97216	162,42	7,130	B4	

Some results that could be interpreted from the table above are as follows:

- Olive Waste

When olive waste was combusted with 5 K/min heating rate, the overall activation energy (E) was 46,79 kJ/mol, frequency factor (log A) was 4,067 and the kinetic model was second order chemical kinetics controlled (Fn2).

It has been observed that between 378-673 K, there was no change in the kinetic parameters and between 673-722 K, E value was 16,68 kJ/mol, log A was 2,535 and kinetic model was D3, three-dimensional diffusion in spherical symmetry. It is visible that as temperature increases, activation energy decreases.

With heating rate 10 K/min, olive waste showed a different behavior. The overall E value was 27,05 kJ/mol, log A was 3,900 and the kinetic model was second order chemical kinetics controlled (Fn2).

Between 378-673 K, E value was 10,30 kJ/mol, log A was 2,402 and the kinetic model was third order chemical kinetics controlled (Fn3). Between 673-773 K, E value was 37,44 kJ/mol, log A was 3,357 and kinetic model was branching core model (B4). Between 773-873 K, E value was 45,23 kJ/mol, log A was 3,849 and kinetic model was branching core model (B4). Between 873-978 K, E value was 54,46 kJ/mol, log A was 4,262 and kinetic model was again branching core model (B4).

With increasing temperature, E values decreased with 5 K/min heating rate and increased in 10 K/min heating rate. As olive waste is the poorest by means of volatile matter content, less volatiles leaving the sample results in less porosity and it is very logical that higher activation energies are observed at high temperatures. Besides, ash content is the reason that the highest E value is observed in the highest temperature range in this sample. Though inorganic components sometimes have catalytic effects on the reaction, usually they require very high E values during decomposition [2].

Olive waste has the lowest overall E value at 10 K/min. When heating rate was 5 K/min, this sample had greater E values than most of the samples. The decrease in E values with increasing heating rate may be due to the decrease in the effect of the limiting conditions like resistance to heat and mass transfer.

For 5 K/min, log A values varied between 2,535-4,067 and for 10 K/min, they varied between 2,402-4,262. Up to 673 K, the combustion mechanism was chemical kinetics

controlled and later it changed to branching core. Total combustion time was 68 min. for 5 K/min heating rate and 64 min. for 10 K/min. The lower heating rate causes longer combustion time, the mass change rate stops at a lower temperature and an increase in E value is observed.

- Sunflower Seed Shell

When sunflower seed shell was combusted with 5 K/min heating rate, the overall E value was 39,98 kJ/mol, log A was 3,613 and the kinetic model was second order chemical kinetics controlled (Fn2).

Between 378-673 K, E value was 17,81, log A was 2,723 and mechanism was third order chemical kinetics controlled (Fn3). Between 673-773 K, E value was 10,52 kJ/mol, log A was 1,306 and kinetic model was D4, three-dimensional diffusion in cylindrical symmetry. Between 773-818 K, E value was 11,41 kJ/mol, log A was 1,733 and kinetic model was D4, three-dimensional diffusion in cylindrical symmetry.

In the same manner with olive waste, kinetic parameters of the lower heating rate decrease as temperature increases. The combustion time increases and combustion is completed at a lower temperature. The kinetic model was chemical kinetics controlled below 673 K and diffusion controlled above that.

With heating rate 10 K/min, the overall E value was 40,52 kJ/mol, log A was 3,871 and the kinetic model was second order chemical kinetics controlled (Fn2).

Between 378-673 K, E value was 17,34 kJ/mol, log A was 2,99 and the kinetic model was third order chemical kinetics controlled (Fn3). Between 673-773 K, E value was 49,22 kJ/mol, log A was 4,304 and kinetic model was branching core model (B4). Between 773-903 K, E value was 21,16 kJ/mol, log A was 2,650 and kinetic model was branching core model (B1).

The increase in the heating rate decreased the reaction time. Like in olive waste but only up to 773 K, the increasing temperature increased the E values and after 773 K, lower E values have been observed. Combustion mechanism was chemical kinetics controlled below 673 K and branching core between 673-903 K. For 5 K/min, log A values varied between 1,306-3,613 and for 10 K/min, they varied between 2,650-4,304. Total combustion time was 88 min. for 5 K/min heating rate and 52 min. for 10 K/min.

In olive waste and sunflower seed shell experiments, with lower heating rate, E values decreased with increasing temperature and with higher heating rate, increasing temperature also increase E. The reason is that, with the higher heating rate, lignin decomposition occurs at higher temperatures and this results in higher E values.

- Rapeseed

When rapeseed was combusted with 5 K/min heating rate, the overall E value was 51,79 kJ/mol, log A was 4,144 and the kinetic model was branching core (B4).

Between 378-673 K, E value was 41,78, log A was 3,702 and mechanism was third order chemical kinetics controlled (Fn3). Between 673-773 K, E value was 16,19 kJ/mol, log A was 1,926 and kinetic model was D2, two-dimensional diffusion controlled.

In the same manner with olive waste and sunflower seed shell, E value and the final temperature of the lower heating rate decrease as temperature increases. Combustion mechanism was branching core and chemical kinetics controlled up to 673 K and diffusion controlled above that.

With heating rate 10 K/min, the overall E value was 86,01 kJ/mol, log A was 5,155 and the kinetic model was branching core model (B4).

Between 378-673 K, E value was 9,80 kJ/mol, log A was 2,347 and the kinetic model was third order chemical kinetics controlled (Fn3). Between 673-773 K, E value was 15,43 kJ/mol, log A was 2,349 and kinetic model was branching core (B4). Between 773-873 K, E value was 16,91 kJ/mol, log A was 2,466 and kinetic model was branching core model (B4). Between 873-973 K, E value was 22,27 kJ/mol, log A was 2,718 and kinetic model was branching core model (B4). Between 973-1073 K, E value was 78,39 kJ/mol, log A was 4,580 and kinetic model was branching core model (B4). Between 1073-1173 K, E value was 54,26 kJ/mol, log A was 2,980 and kinetic model was three-dimensional diffusion in cylindrical symmetry (D4).

The combustion mechanism of rapeseed at 10 K/min was chemical kinetics controlled between 378-773 K and branching core in general. For 5 K/min, log A values varied between 1,926-4,144 and for 10 K/min, they varied between 2,347-5,155. Total combustion time was 84 min. for 5 K/min heating rate and 76,4 min. for 10 K/min. An increase in activation energies have been observed with increasing heating rate.

- Walnut Shell

When walnut shell was combusted with 5 K/min heating rate, the overall E value was 59,07 kJ/mol, log A was 4,591 and the kinetic model was second order chemical kinetics controlled (Fn2).

The combustion reaction of walnut shell with 5 K/min heating rate was completed at 723 K and the mechanism was chemical kinetics controlled. Combustion time was longer than it was for 10 K/min. Combustion of the sample was completed within a low temperature range therefore it was not investigated within intervals.

With heating rate 10 K/min, the overall E value was 51,71 kJ/mol, log A was 4,379 and the kinetic model was second order chemical kinetics controlled (Fn2).

Between 378-673 K, E value was 59,55 kJ/mol, log A was 4,839 and the kinetic model was second order chemical kinetics controlled (Fn2). Between 673-873 K, E value was 25,18 kJ/mol, log A was 2,490 and kinetic model was three-dimensional diffusion in spherical symmetry (D3).

The combustion mechanism of walnut shell at 10 K/min was chemical kinetics controlled up to 673 K. For 5 K/min, log A value was 4,591 and for 10 K/min, they varied between 2,490-4,839. Total combustion time was 68 min. for 5 K/min heating rate and 50 min. for 10 K/min.

- Pine Conifer

When pine conifer was combusted with 5 K/min heating rate, the overall E value was 59,22 kJ/mol, log A was 4,529 and the kinetic model was second order chemical kinetics controlled (Fn2).

Between 378-673 K, E value was 56,04 kJ/mol, log A was 4,380 and mechanism was second order chemical kinetics controlled (Fn2). Between 673-748 K, E value was 19,23 kJ/mol, log A was 2,144 and kinetic model was D2, two-dimensional diffusion controlled.

Similar to the previous samples, the lower heating rate resulted in the decrease of E values and increase in combustion time with increasing temperature. Combustion mechanism was chemical kinetics controlled up to 673 K and diffusion controlled above that.

With heating rate 10 K/min, the overall E value was 46,83 kJ/mol, log A was 4,057 and the kinetic model was second order chemical kinetics controlled (Fn2).

Between 378-673 K, E value was 59,64 kJ/mol, log A was 4,780 and the kinetic model was second order chemical kinetics controlled (Fn2). Between 673-773 K, E value was 52,56 kJ/mol, log A was 4,266 and kinetic model was branching core (B4). Between 773-873 K, E value was 77,71 kJ/mol, log A was 5,153 and kinetic model was branching core (B4). Between 873-973 K, E value was 15,32 kJ/mol, log A was 1,810 and kinetic model was diffusion controlled (D4).

Up to 773 K, E values decrease with the increasing temperature, between 773-873 K, E values increase with increasing temperature and above 873 K, a decrease in E values were observed. The overall combustion mechanism was chemical kinetics controlled. For 5 K/min, log A values varied between 2,144-4,529 and for 10 K/min, they varied between 1,810-5,153. Total combustion time was 74,4 min. for 5 K/min heating rate and 60,8 min. for 10 K/min. Increase in the heating rate results in a decrease in combustion time.

- Tea Residue

When tea residue was combusted with 5 K/min heating rate, the overall E value was 68,60 kJ/mol, log A was 4,268 and the kinetic model was three-dimensional diffusion in cylindrical symmetry (D4).

Between 378-673 K, there was no change in the kinetic parameters. Between 673-773 K, E value was 59,38 kJ/mol, log A was 4,182 and kinetic model was branching core model (B4). Between 773-873 K, E value was 22,51 kJ/mol, log A was 2,346 and kinetic model was again branching core model (B4). Between 873-973 K, E value was 33,24 kJ/mol, log A was 2,317 and kinetic model was three-dimensional diffusion in cylindrical symmetry (D4).

In combustion reactions with lower heating rate, combustion time of tea residue was longer and whole reaction was diffusion controlled except for branching core model between 673-873 K. In the previous samples, mechanisms were chemical kinetics controlled up to 673 K. Up to 873 K, the E values, in ordinance with other samples, decreases with increasing temperature at lower heating rate. Above 873 K, E values increase.

With heating rate 10 K/min, the overall E value was 95,63 kJ/mol, log A was 5,636 and the kinetic model was branching core model (B4).

Between 378-673 K, E value was 43,73 kJ/mol, log A was 4,103 and the kinetic model was second order chemical kinetics controlled (Fn2). Between 673-773 K, E value was 55,51 kJ/mol, log A was 4,484 and kinetic model was third order chemical kinetics controlled (Fn3). Between 773-873 K, E value was 44,31 kJ/mol, log A was 3,721 and kinetic model was branching core model (B4). Between 873-1021 K, E value was 17,99 kJ/mol, log A was 2,110 and kinetic model was two-dimensional diffusion (D2).

The overall combustion mechanism of tea residue at 10 K/min was appropriate with the branching core model, except for chemical kinetics controlled between 378-773 K. For 5 K/min, log A values varied between 2,317-4,268 and for 10 K/min, they varied between 2,110-5,636. Total combustion time was 108,4 min. for 5 K/min heating rate and 64 min. for 10 K/min. Combustion takes longer with low heating rates. The general trend is that E values decrease with increasing temperature but within the temperature interval of 673-773 K, E values increase.

The different behavior of E values with increasing temperature depends on the differences in their structural composition.

- Cotton Residue

When cotton residue was combusted with 5 K/min heating rate, the overall E value was 162,20 kJ/mol, log A was 8,39 and the kinetic model was branching core model (B4).

Between 378-673 K, E value was 47,95 kJ/mol, log A was 3,954 and kinetic model was second order chemical kinetics controlled (Fn2). Between 673-773 K, E value was 36,58 kJ/mol, log A was 2,713 and kinetic model was three-dimensional diffusion (D3). Between 773-813 K, E value was 101,48 kJ/mol, log A was 5,059 and kinetic model was three-dimensional diffusion (D3).

The highest E value of the experiments with 5 K/min heating rate belongs to cotton residue.

With heating rate 10 K/min, the overall E value was 108,94 kJ/mol, log A was 6,166 and the kinetic model was branching core model (B4).

Between 375-673 K, E value was 43,97 kJ/mol, log A was 4,064 and the kinetic model was second order chemical kinetics controlled (Fn2). Between 673-773 K, E value was 41,22 kJ/mol, log A was 3,68 and kinetic model was branching core model (B4). Between 773-873 K, E value was 48,79 kJ/mol, log A was 3,97 and kinetic model was branching core model (B4). Between 873-973 K, E value was 69,51 kJ/mol, log A was 4,68 and kinetic model was branching core model (B4).

For 5 K/min, log A values varied between 2,713-8,390 and for 10 K/min, they varied between 3,680-6,166. Total combustion time was 86 min. for 5 K/min heating rate and 68 min. for 10 K/min. Combustion takes longer with low heating rates. At both heating rates, between 673-773 K, E values decrease.

- Grape seed

When grape seed was combusted with 5 K/min heating rate, the overall E value was 135,78 kJ/mol, log A was 7,17 and the kinetic model was branching core model (B4).

Between 378-673 K, E value was 41,57 kJ/mol, log A was 3,604 and kinetic model was second order chemical kinetics controlled (Fn2). Between 673-773 K, E value was 23,26 kJ/mol, log A was 2,431 and kinetic model was branching core model (B4). Between 773-873 K, E value was 15,79 kJ/mol, log A was 1,833 and kinetic model was two-dimensional diffusion (D2).

The E values, in ordinance with other samples, decreases with increasing temperature at lower heating rate.

With heating rate 10 K/min, the overall E value was 117,17 kJ/mol, log A was 6,360 and the kinetic model was branching core model (B4).

Between 378-673 K, E value was 44,45 kJ/mol, log A was 4,025 and the kinetic model was second order chemical kinetics controlled (Fn2). Between 673-773 K, E value was 38,63 kJ/mol, log A was 3,505 and kinetic model was branching core model (B4). Between 773-873 K, E value was 57,97 kJ/mol, log A was 4,245 and kinetic model was branching core model (B4). Between 873-1013 K, E value was 12,06 kJ/mol, log A was 1,553 and kinetic model was three-dimensional diffusion (D4).

For 5 K/min, log A values varied between 1,833-7,170 and for 10 K/min, they varied between 1,553-6,360. Total combustion time was 96,8 min. for 5 K/min heating rate

and 68 min. for 10 K/min. Combustion takes longer with low heating rates. E values decrease with increasing temperature except for 773-873 K where there is an increase.

- Hybrid Poplar

When hybrid poplar was combusted with 5 K/min heating rate, the overall E value was 66,81 kJ/mol, log A was 4,960 and the kinetic model was second order chemical kinetics controlled (Fn2). Combustion of hybrid poplar was completed at a low temperature so it was not examined within intervals.

With heating rate 10 K/min, the overall E value was 41,69 kJ/mol, log A was 3,911 and the kinetic model was second order chemical kinetics controlled (Fn2).

Between 378-673 K, E value was 64,40 kJ/mol, log A was 4,960 and the kinetic model was second order chemical kinetics controlled (Fn2). Between 673-773 K, E value was 53,43 kJ/mol, log A was 4,440 and kinetic model was branching core model (B4). Between 773-903 K, E value was 11,73 kJ/mol, log A was 1,64 and kinetic model was three-dimensional diffusion in cylindrical symmetry (D4). Combustion occurred with lower E values above 673 K due to the fact that hybrid poplar has the highest volatile matter content and relatively low fixed C content. When volatile matter leaves the biomass body, diffusion through the porous media left behind controls reaction.

For 5 K/min, log A value was 4,960 and for 10 K/min, they varied between 1,640-4,960. Total combustion time was 66 min. for 5 K/min heating rate and 52 min. for 10 K/min.

- Sour Cherry Stone

When sour cherry stone sample was combusted with 5 K/min heating rate, the overall E value was 42,61 kJ/mol, log A was 3,711 and the kinetic model was second order chemical kinetics controlled (Fn2).

Between 373-673 K, E value was 44,95 kJ/mol, log A was 3,854 and kinetic model was again second order chemical kinetics controlled (Fn2). Between 673-773 K, E value was 12,42 kJ/mol, log A was 1,676 and kinetic model was two-dimensional diffusion controlled (D2).

The decreasing behavior of E value with increasing temperature at a lower heating rate was again observed in sour cherry stone.

With heating rate 10 K/min, the overall E value was 29,18 kJ/mol, log A was 3,163 and the kinetic model was second order chemical kinetics controlled (Fn2).

Between 378-673 K, E value was 46,51 kJ/mol, log A was 4,180 and the kinetic model was second order chemical kinetics controlled (Fn2). Between 673-773 K, E value was 33,12 kJ/mol, log A was 3,360 and kinetic model was branching core model (B4).

Between 773-873 K, E value was 35,69 kJ/mol, log A was 3,45 and kinetic model was branching core model (B4). Between 873-973 K, E value was 65,25 kJ/mol, log A was 4,49 and kinetic model was branching core model (B4). Between 973-1058 K, E value was 162,42 kJ/mol, log A was 7,130 and kinetic model was branching core model (B4).

For 5 K/min, log A values varied between 1,676-3,854 and for 10 K/min, they varied between 3,163-7,130. Total combustion time was 76 min. for 5 K/min heating rate and 70 min. for 10 K/min.

Again, at lower heating rate, combustion took longer. At both heating rates, reaction was chemical kinetics controlled up to 673 K.

7- OVERALL RESULTS AND RECOMMENDATIONS

The kinetic parameters (activation energy (E), log A) and kinetic models were determined by Coats-Redfern method and the relationships between these parameters and the data from DTG curves have also been compared.

The results are:

- At 5 K/min heating rate, the E values of the samples except for tea and cotton residues decrease as the temperature increases.
- At 5 K/min heating rate, the combustion mechanisms of the samples excluding tea residue, rapeseed, grapeseed and cotton residue are chemical kinetics controlled up to 673 K.
- At 5 K/min heating rate, at temperatures above 673 K, the mechanism is branching core or diffusion controlled.
- The combustion times of samples at 5 K/min heating rate varied between 66-108,4 min and varied between 50-76,4 min. for 10K/min heating rate. The increase in the heating rate resulted in a decrease in combustion time.
- For 5 K/min the maximum combustion rates of the samples varied between 1-1,7 and for 10 K/min they varied between 1,8-4,05. The increase in heating rate also increased the maximum burning rates.
- The temperatures at which maximum burning rate is observed varied between 483-531 K for 5 K/min and between 474-518 K for 10 K/min, the increase in heating rate decreased the temperature range of the maximum burning rates.
- For 5 K/min log A values varied between 1,306-8,400 and for 10 K/min, they varied between 1,553-7,130.
- For 10 K/min heating rate, although the general trend is that E values decrease with increasing temperature, between 673-873 K, an increase in E values have been observed.

The recommendations are:

- Analysis of the combustion gases should be carried out and the data obtained should also be examined to clarify combustion mechanisms.
- Effects of higher heating rates on the combustion mechanisms should be investigated.
- The characteristics of biomass samples, combustion conditions and the kinetic parameters evaluated should be collected in a database and should be kept up-to-date.
- The idea of burning adequate biomass mixtures might be a solution to provide homogeneity.
- Emissions of combustion should be examined with an environmental view.
- Melting temperature of the ash should be known well as ash formation causes problems in industrial scale systems.

REFERENCES

[1] **Meteoğlu, M.,** 2005. Investigation of the combustion kinetics of some biomass types, *M.Sc Thesis*, I.T.U. Institute of Science and Letters, Istanbul.

[2] **Quaak, P., Knoef, H. and Stassen, H.,** 1999. Energy from biomass: a review of combustion and gasification technologies, World Bank technical paper, 422 Energy Series, World Bank,Washington D.C.

[3] **Klass, D.L.,** 1998. Biomass for Renewable Energy, Fuels, Chemicals, Academic Press, Sandiego.

[4] **Lans, R.P., Pedersen, L.T., Jensen, A., Glarborg, P. and Dam-Johansen, K.,** 2000. Modeling and experiments of straw combustion in a grate furnace, *Biomass and Bioenergy*, **19**, 199-208.

[5] **Bain, R.L.,** 2004. An introduction to biomass thermochemical conversion, DOE/NASLUGC Biomass and Solar Energy Workshops, August 3-4.

[6] **Mansaray, K.G. and Ghaly, A.E.,** 1999. Determination of kinetic parameters of rice husks in oxygen using thermogravimetric analysis, *Biomass and Bioenergy*, **17**, 19-31.

[7] **Dare, P., Gifford, J., Hooper, R.J., Clemens, A.H., Damiano, L.F., Gong, D. and Matheson, T.W.,** 1999. Combustion performance of biomass residue and purpose grown species, *Biomass and Bioenergy*, **21**, 277-287.

[8] **Hustad, J.E., Skreiberg, O. and Sonju, O.K.,** 1995. Biomass combustion research and utilization in IEA countries, *Biomass and Bioenergy*, **9**, 235-255.

[9] **Dornburg, V. and Faaij, A.P.C.,** 2001. Efficiency and economy of wood-fired biomass energy systems in relation to scale regarding heat and power generation using combustion and gasification technologies, *Biomass and Bioenergy*, **21**, 91-108.

[10] **Jones, J.M., Pourkashanian, M., Williams, A. and Hainsworth, D.,** 2000. A comprehensive biomass combustion model, *Renewable Energy*, **19**, 229-234.

[11] **Broek, R.V.D., Faaij, A. and Wijk, A.V.,** 1996. Biomass combustion for power generation, *Biomass and Bioenergy*, **11**, 271-281.

[12] **Wereko-Brobby, C. and Hagan, E.B.,** 1996. Biomass conversion and technology, Unesco Energy Engineering Series, Wiley, Chichester.

[13] **Blander, M., Ragland, K.W., Cole, R.L., Libera, J.A. and Pelton, A.,** 1995. The inorganic chemistry of wood combustion for power production, *Biomass and Bioenergy*, **8**, 29-38.

[14] **Lapuerta, M., Hernandez, J.J. and Rodriguez, J.,** 2004. Kinetics of devolatilisation of forestry wastes from thermogravimetric analysis, *Biomass and Bioenergy*, **27**, 385-391.

[15] **Prasad, V.K., Kant, Y., Gupta, P.K., Sharma, C., Mitra, A.P. and Badarinath, K.V.S.,** 2001. Biomass and combustion characteristics of secondary

mixed deciduous forests in Eastern Ghats of India, *Atmospheric Environment*, **35**, 3085-3095.

[16] **Lindsey, B.,** 2004. Thermogravimetric analysis of biomass and lignites for co-combustion, PhD End of the Year Report, University of Bath, UK.

[17] **Biomass Energy**
http://www.ecology.com/archived-links/biomass-energy/index.html
15.11.2005

[18] **Yu-qi, J., Jian-hua, Y. and Ke-fa, C.,** 2004. Study on the comprehensive combustion kinetics of MSW, *Journal of Zhejiang University Science*, **5**, 283-289.

[19] **Wu, C., Chang, C., Lin, J. and Hwang, J.,** 1997. Thermal treatment of coated printing and writing paper in MSW: pyrolysis kinetics, *Fuel*, **76**, 1151-1157.

[20] **Wang, S., Slovak, V. and Haynes, B.S.,** 2005. Kinetic studies of graphon and coal-char reaction with NO and O_2: direct non-linear regression from TG curves, *Fuel Processing Technology*, **86**, 651-660.

[21] **Heikkinen, J.M., Hordijk J.C., Jong, W. and Spliethoff H.,** 2004. Thermogravimetry as a tool to classify waste components to be used for energy generation, *Analytical and Applied Pyrolysis, J.*, **71**, 883-900.

[22] **Orfao, J.J.M., Antunes, F.J.A. and Figueiredo, J.L.,** 1999. Pyrolysis kinetics of lignocellulosic materials-three independent reactions model, *Fuel*, **78**, 349-358.

[23] **Saade R.G. and Kozinski, J.A.,** 2000. Numerical modeling and TGA/FTIR/GCMS investigation of fibrous residue combustion, *Biomass and Bioenergy*, **18**, 391-404.

[24] **Biomass Types**
http://www.esru.strath.ac.uk/EandE/Web_sites/03-04/biomass/background%20info4.html
09/09/2005

[25] **Gangavati, P.B., Safi, M.J., Singh, A., Prasad, B. and Mishra, I.M.,** 2005. Pyrolysis and thermal oxidation kinetics of sugar mill press mud, *Thermochimica Acta*, **428**, 63-70.

[26] **Chen, J.H., Chen, K.S. and Tong, L.Y.,** 2001. On the pyrolysis kinetics of scrap automotive tires, *Hazardous Materials, J.*, **B84**, 43-55.

[27] **Pritchard, D.,** 2002, Biomass combustion gas turbine CHP, *UK Department of Trade and Industry Report for Talbott's Heating Ltd*, UK.
www.dti.gov.uk/energy/renewables/ publications/pdfs/bu100679.pdf
3/11/2005

[28] **Beddingham Experimental Shaft Kiln**
http://www.subbrit.org.uk/sb-sites/sites/b/beddingham_cement_kiln/index.shtml
05.12.2005

[29] **Biogas and Liquid Biofuels**
http://www.itdg.org/docs/technical_information_service/biogas_liquid_fuels.pdf
14.12.2005

[30] **The research progress of biomass pyrolysis processes**
http://www.fao.org/docrep/T4470E/t4470e0a.htm
10/11/2005

[31] **Zahritz, W.H. and Mimbela, L.E.,** 2000. Feasibility study of a biomass power plant cofired with natural gas for the village of Angel Fire, *Western Regional Biomass Energy Program Final Report*, New Mexico.
http://www.westbioenergy.org/angelfire.htm#_Toc495400515
30/10/2005.

[32] **Fluidized Bed Furnace**
http://nett21.gec.jp/JSIM_DATA/WASTE/WASTE_5/html/Doc_509_1.html
12/09/2005

[33] **Tillman, D.A.,** 2000. Biomass co-firing:the technology, the experience, the combustion consequences, *Biomass and Bioenergy*, **19**, 365-384.

[34] **Gaur, S., Reed, T.B.,** 1994. Prediction of cellulose decomposition rates from thermogravimetric data, *Biomass and Bioenergy*, **7,** 61-67.

[35] **Slovak V.,** 2001. Determination of kinetic parameters by direct non-linear regression from TG curves, *Thermochimica Acta*, **372**, 175-182.

[36] **Wang, X., Yang, K., Wang, Y., Wu, B., Liu, Y. and Yang, B.,** 2003. Thermogravimetric analysis of the decomposition of poly(1,4-dioxan-2-one) starch blends, *Polymer Degradation and Stability*, **81**, 415-421.

[37] **Açma, H.,** 1998. The effect of the mineral content of coal on its combustion properties, *PhD Thesis*, ITU Institute of Science and Letters, Istanbul.

[38] **Coats, A.W. and Redfern, J.P.,** 1964. Kinetic parameters from thermogravimetric data, *Nature*, **201**, 68-69.

[39] **Tonbul, Y., Yurdakoç, K.,** 2001. Thermogravimetric investigation of the dehydration kinetics of KSF, K10 and Turkish bentonite, *Turkish Journal and Chemistry*, 25, 333-339.

[40] **Exploitation of agricultural residues in Turkey**
http://www.agrowaste-tr.org/ablife/index.php?PHPSESSID=ac9dc7b2357949163f483614537dbd5a
01/12/2005

[41] **Turkish Ministry of Agriculture, in Turkish**
http://www.tarim.gov.tr/arayuz/6/icerik.asp?fl=uretim/istatistikler/istatistikler.htm
01/12/2005

[42] **Çaykur**
http://www.caykur.gov.tr/detay.asp?id=45
01/12/2005

[43] **Kataki, R. and Konwer, D.,** 2001. Fuelwood characteristics of some indigenous woody species of north-east India, *Biomass and Bioenergy*, **20**, 17-23.

[44] **Mendez, L.B., Borrego, A.G., Martinez-Tarazona, M.R. and Menendez, R.,** 2003. Influence of petrographic and mineral matter composition of coal particles on their combustion reactivity, *Fuel*, **82**, 1875-1882.

[45] **Werkelin, J., Skrifvars, B.J. and Hupa, M.,** 2005. Ash-forming elements in four Scandinavian wood species. Part I: Summer harvest, *Biomass and Bioenergy*, **29**, 451-466.

[46] **Patumsawad, S. and Cliffe, K.R.,** 2002. Experimental study on fluidized bed combustion of high moisture municipal solid waste, *Energy Conversion and Management*, **43**, 2329-2340.

[47] **Erincin, D., Sınağ, A., Mısırlıoğlu, Z. and Canel, M.,** 2005. Characterization of burning and CO_2 gasification of chars from mixtures of Zonguldak (Turkey) and Australian bituminous coals, *Energy Conversion and Management*, **46**, 2748-2761.

APPENDICES

APPENDIX A

Table A.1: Some kinetic parameters available in the literature

	Sample	E (kJ/mol)	A (min-1)	Heating Rate	Ambient
pine wood	cellulose	88,40	$3,16*10^{7}$	5	N_2, Air
	lignin	18, 1	0,94		
eucalyptus	cellulose	79,40	$5,2*10^{6}$	10	
	lignin	20,20	1,46		
pine bark	cellulose	48,50	$2,44*10^{3}$	5	
	lignin	20,40	0,74		
sugarcane bagasse	hemicellulose	195,00	$4,7*10^{15}$	5	N_2
	cellulose	243,00	$1*10^{18}$		
	lignin	37,00	0,70		
waste wood	hemicellulose	196,90	$4,7*10^{15}$	10	
	cellulose	245,70	$1*10^{18}$		
	lignin	51,40	10,10		
rice husk powder	cellulose	72,70	$3,7*10^{5}$	5	N_2
	lignin	14,10	1,10		
	cellulose	79,10	$2,3*10^{6}$	10	
	lignin	21,90	16,10		
rice husk grain	cellulose	81,80	$2,1*10^{6}$	5	
	lignin	6,30	$8,4*10^{-2}$		
	cellulose	78,70	$1,7*10^{6}$	10	
	lignin	11,50	1,10		
cotton residue char	overall	91,05	$0,19^{-1}$	10	Air
olive kernel char	overall	75,60	$0,042^{-1}$	10	
rice husk cellulose	overall	150,00	1,01	20	O_2
sugarcane bagasse	cellulose	235,00	19,40	10	N_2
	hemicellulose	105,00	9,20		
	lignin	26,00	1,00		
pine sawdust	cellulose	210,00	$1,14*10^{14}$	20	N_2
	hemicellulose	88,40	$5,27*10^{5}$		
	lignin	18,10	0,02		
pine needles	cellulose	69,88	$1,27*10^{5}$	5	Air
	lignin	85,34	$5,98*10^{6}$	10	
sugarcane bagasse	cellulose	235,00	19,40	10	N_2
	hemicellulose	105,00	9,20		
	lignin	26,00	1,00		

APPENDIX B: TG and DTG curves of samples

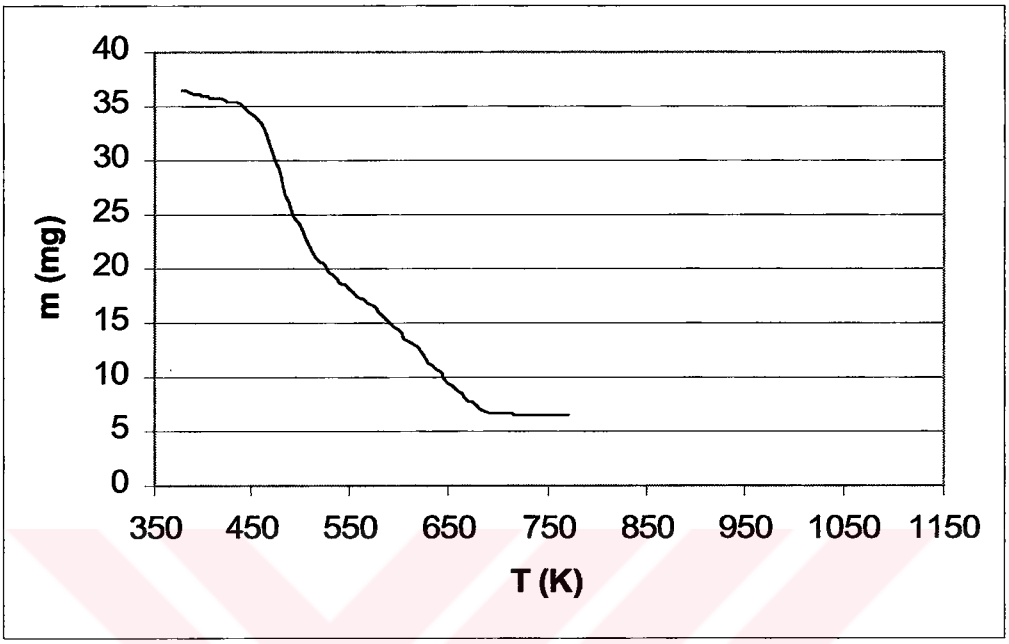

Figure B.1: TG curve of olive waste with heating rate of 5 K/min

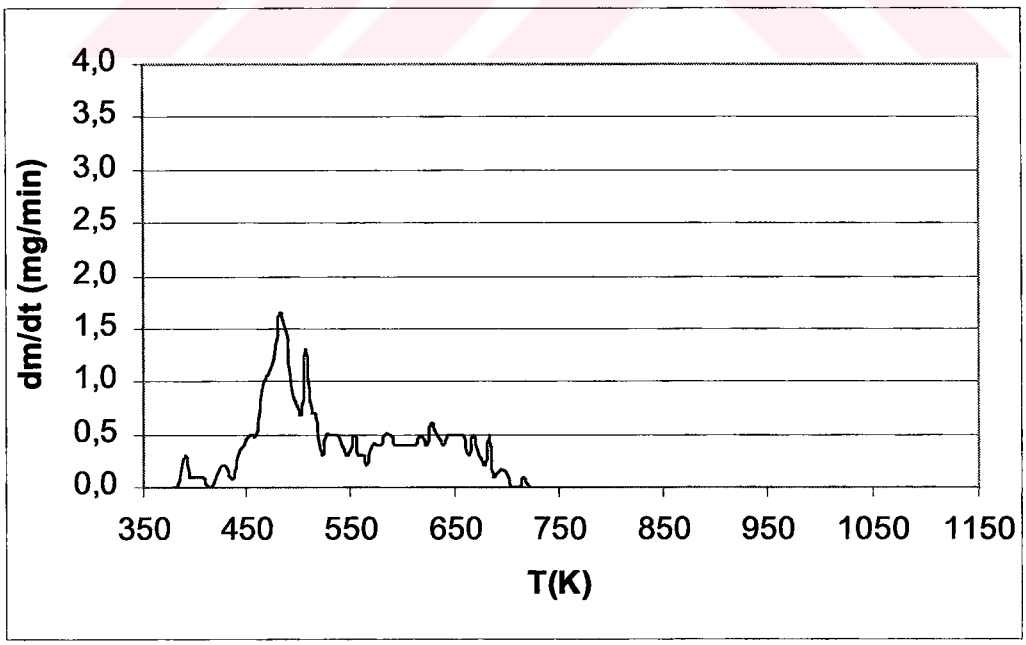

Figure B.2: DTG curve of olive waste with heating rate of 5 K/min

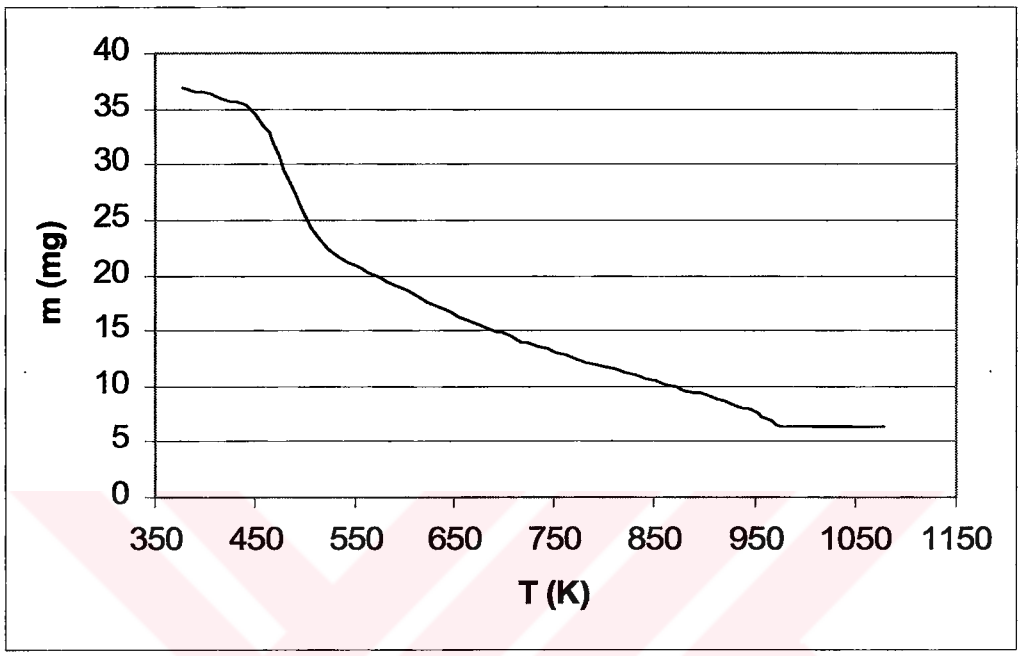

Figure B.3: TG curve of olive waste with heating rate of 10 K/min

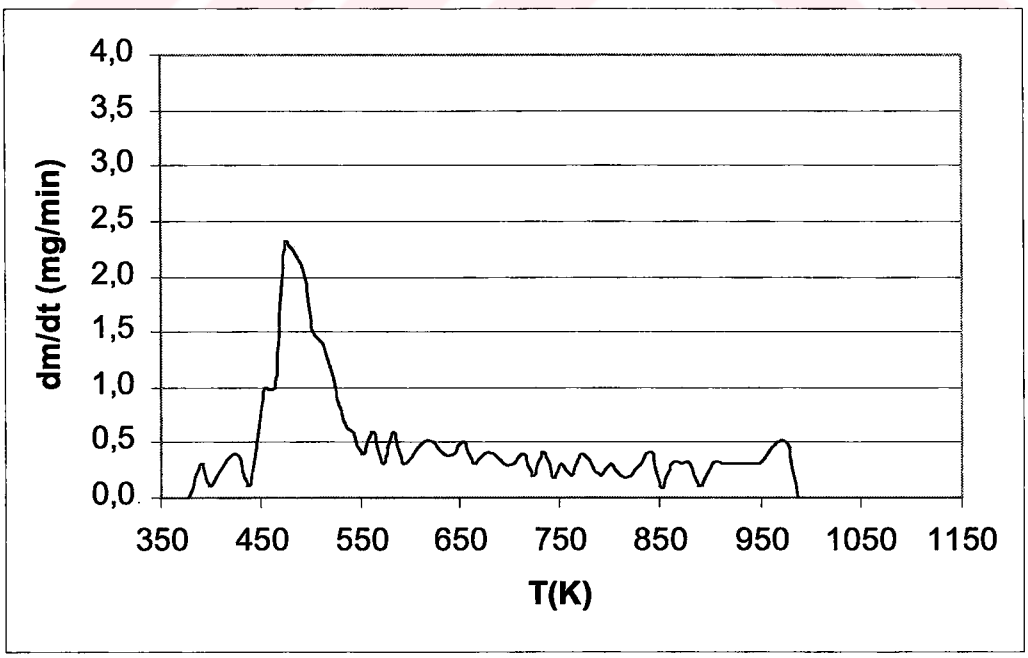

Figure B.4: DTG curve of olive waste with heating rate of 10 K/min

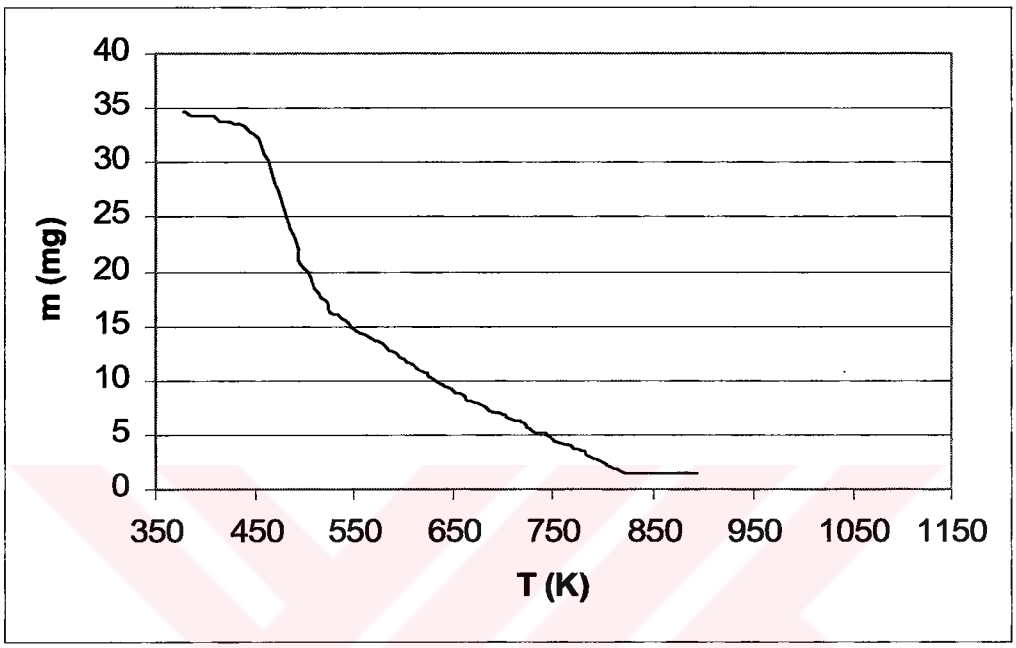

Figure B.5: TG curve of sunflower seed shell with heating rate of 5 K/min

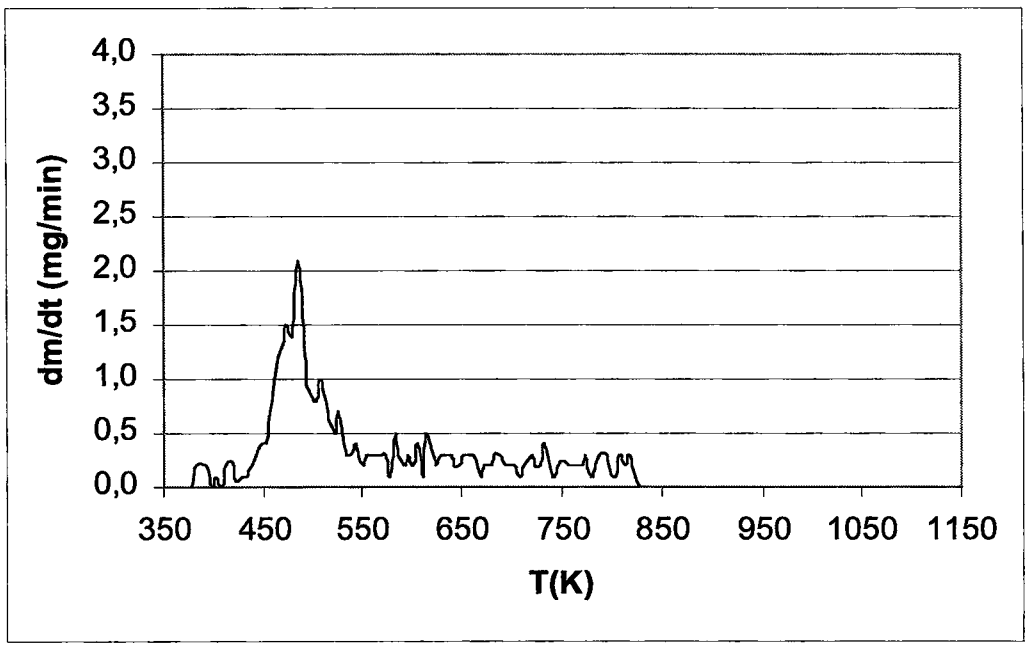

Figure B.6: DTG curve of sunflower seed shell with heating rate of 5 K/min

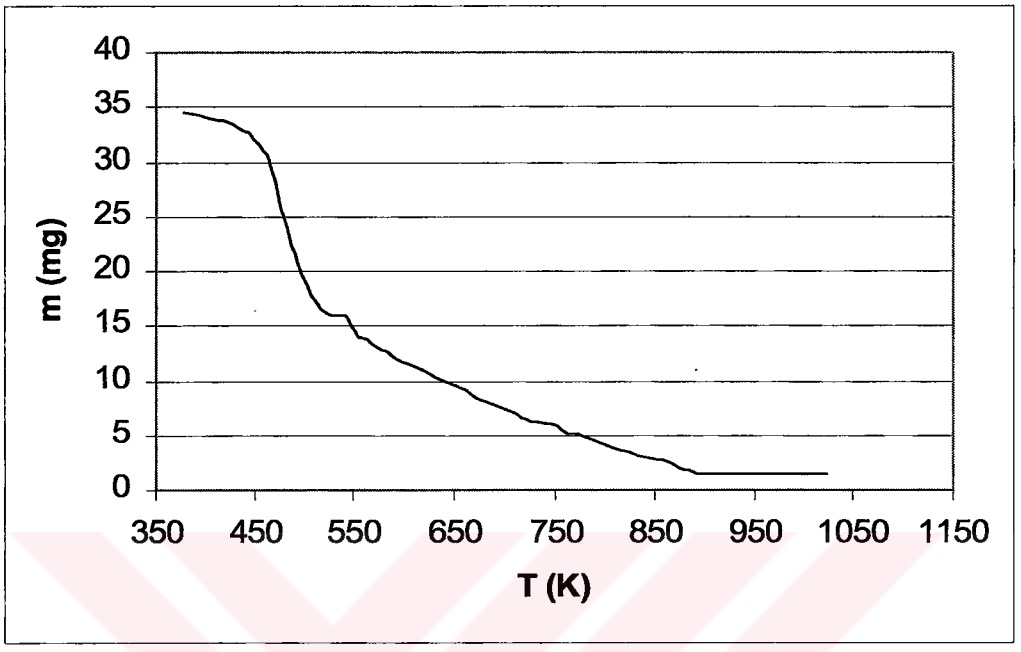

Figure B.7: TG curve of sunflower seed shell with heating rate of 10 K/min

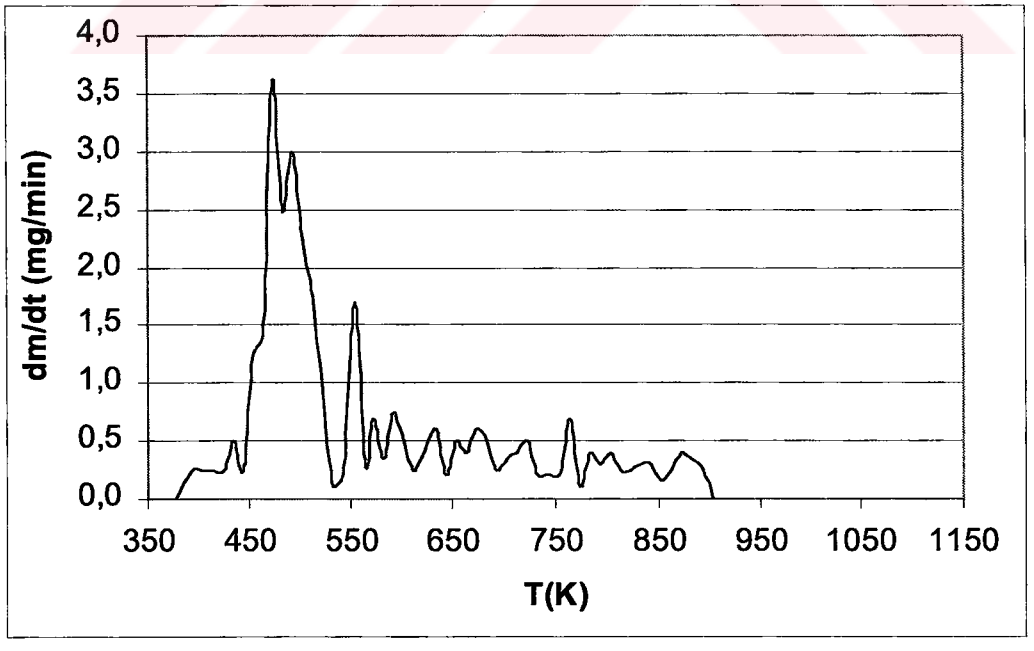

Figure B.8: DTG curve of sunflower seed shell with heating rate of 10 K/min

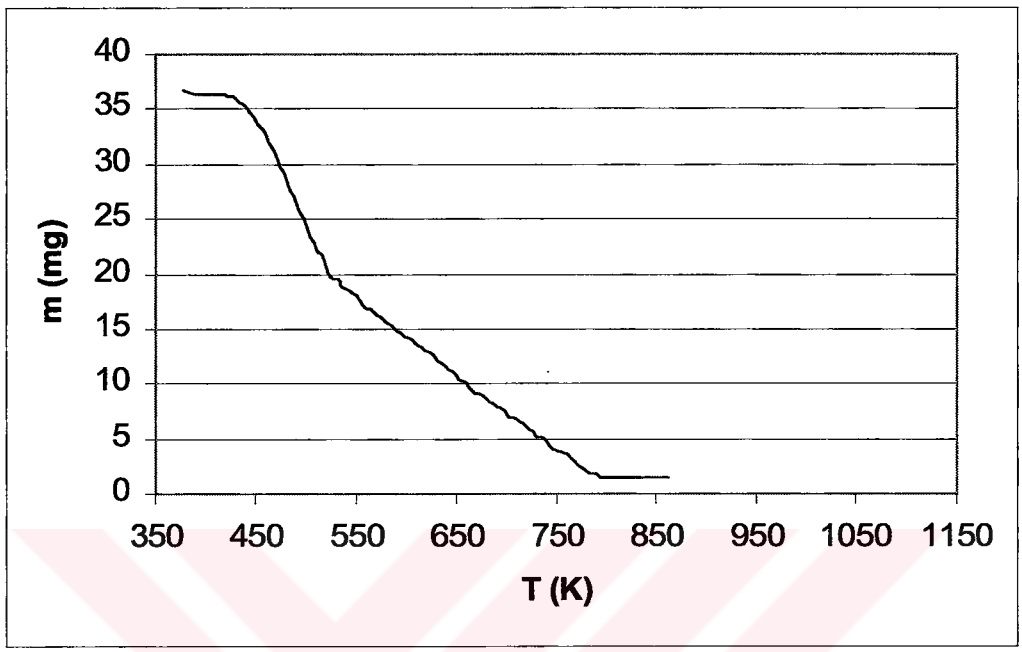

Figure B.9: TG curve of rapeseed with heating rate of 5 K/min

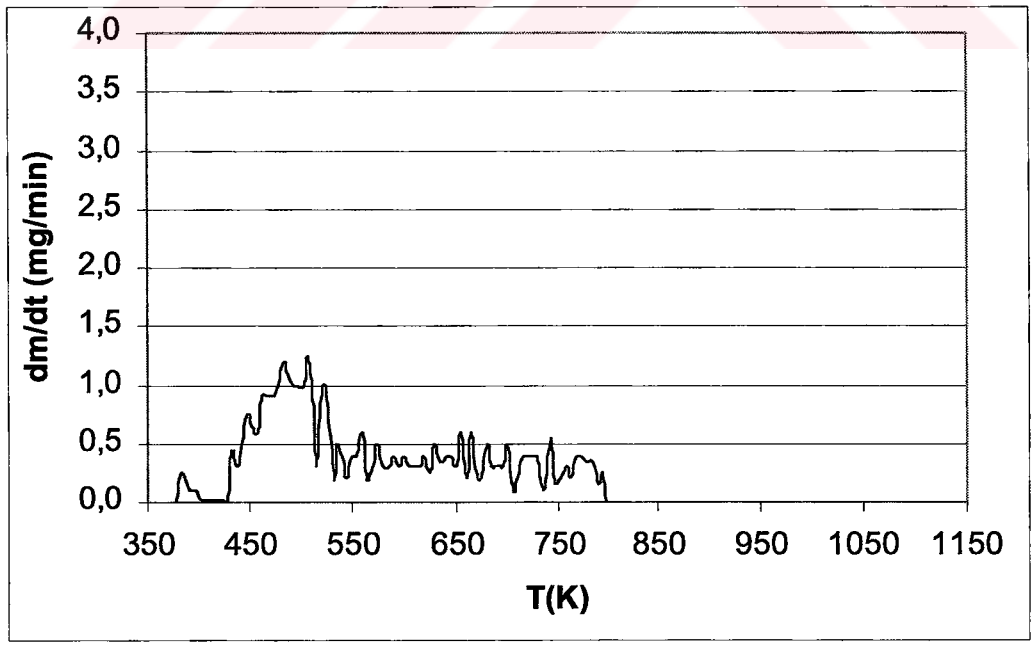

Figure B.10: DTG curve of rapeseed with heating rate of 5 K/min

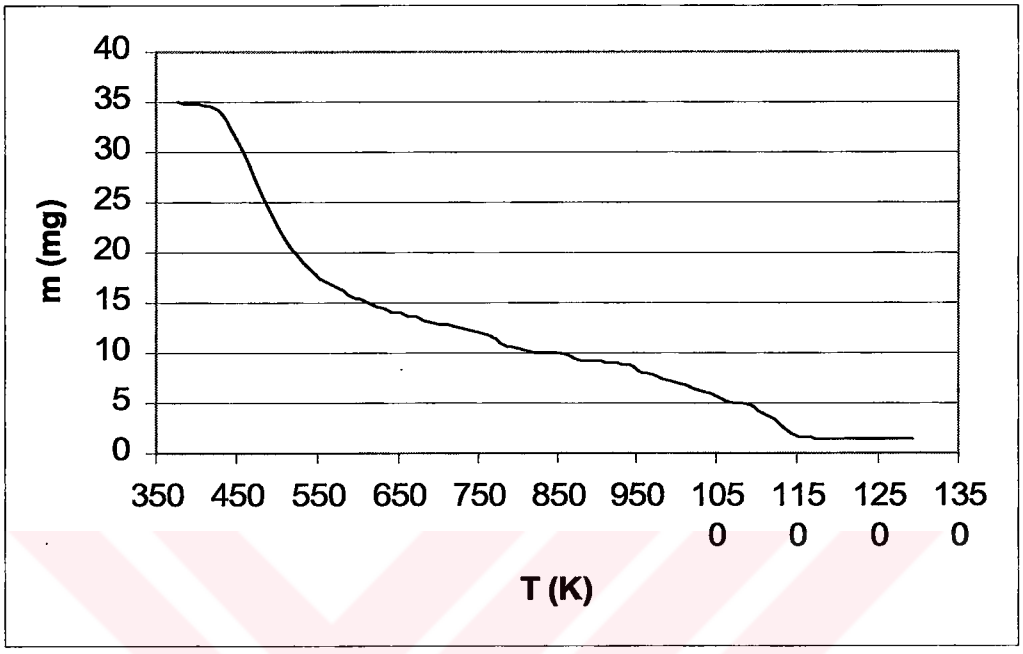

Figure B.11: TG curve of rapeseed with heating rate of 10 K/min

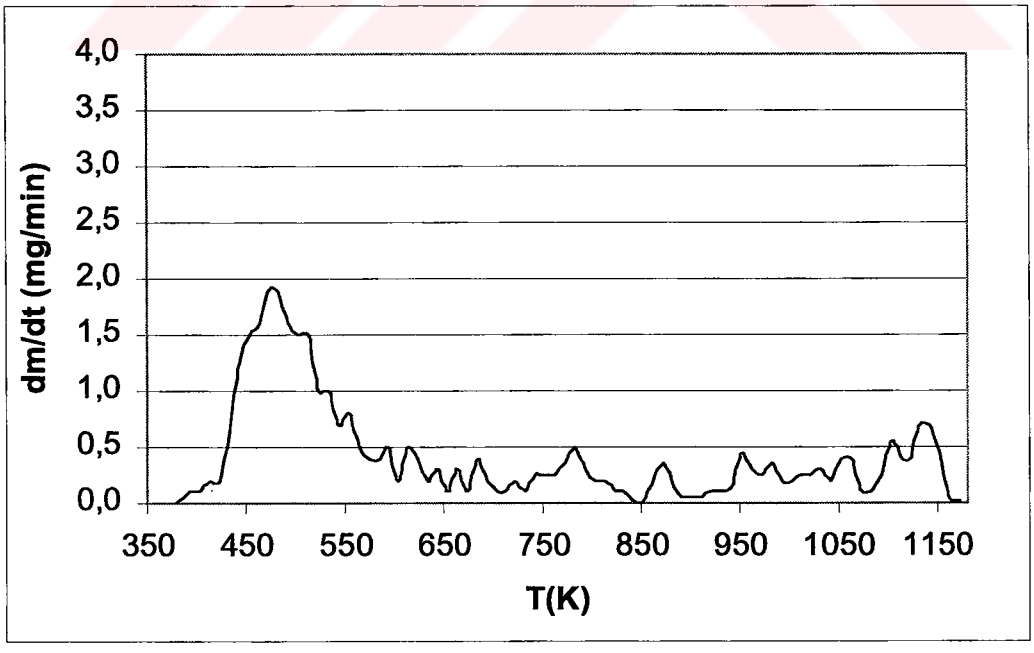

Figure B.12: DTG curve of rapeseed with heating rate of 10 K/min

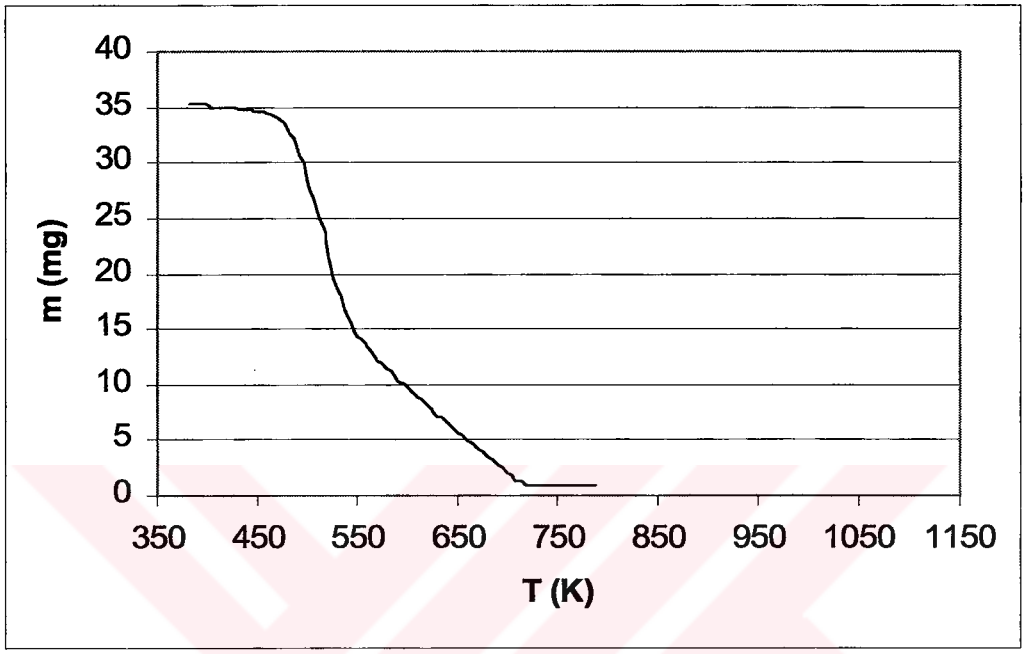

Figure B.13: TG curve of walnut shell with heating rate of 5 K/min

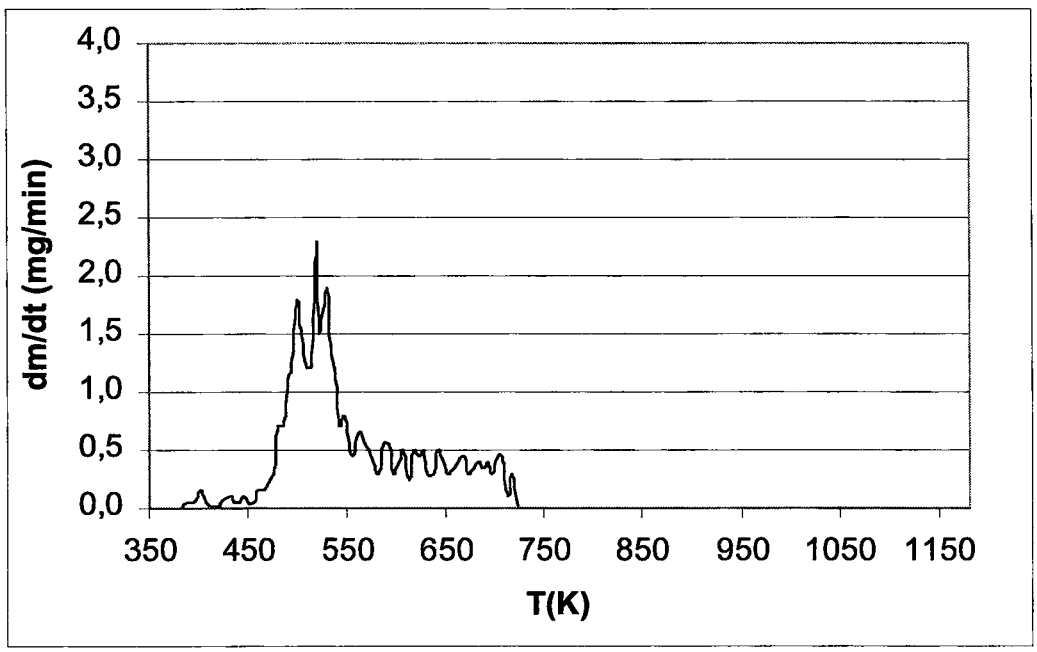

Figure B.14: DTG curve of walnut shell with heating rate of 5 K/min

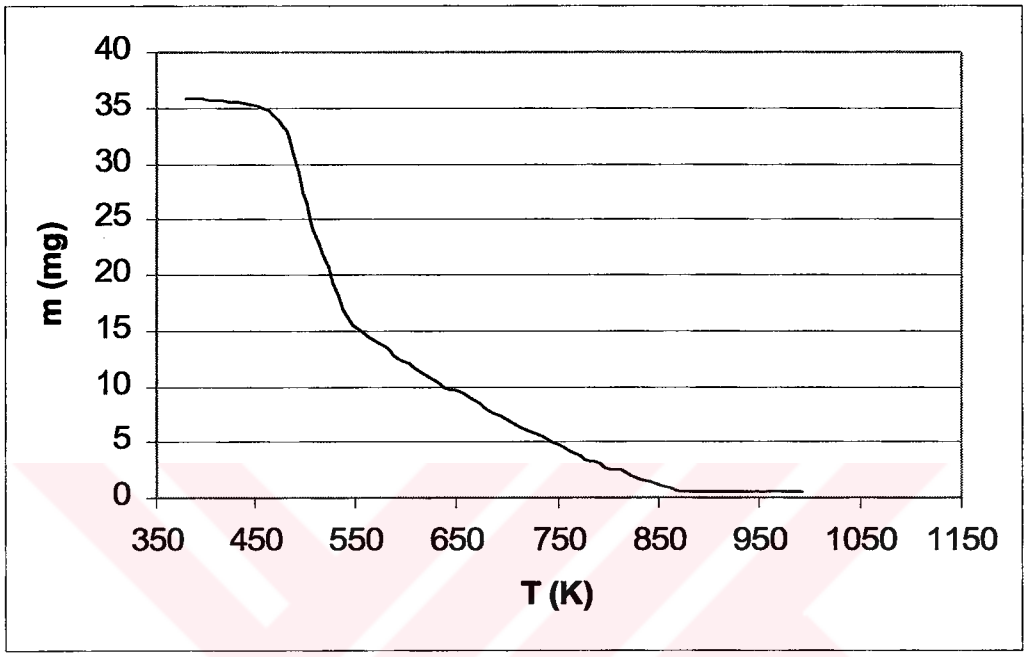

Figure B.15: TG curve of walnut shell with heating rate of 10 K/min

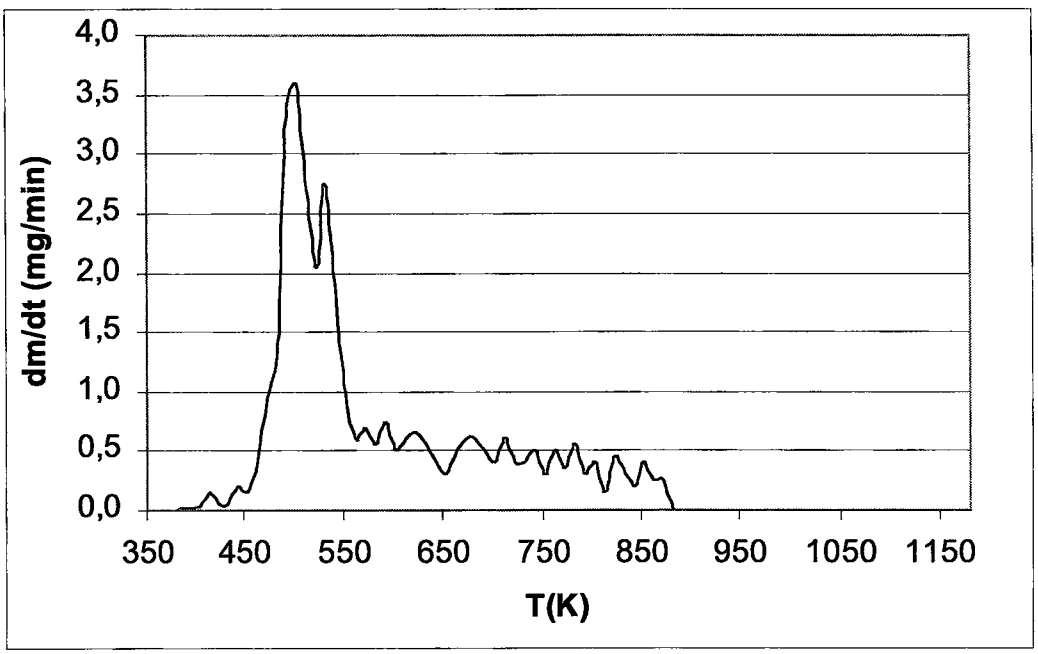

Figure B.16: DTG curve of walnut shell with heating rate of 10 K/min

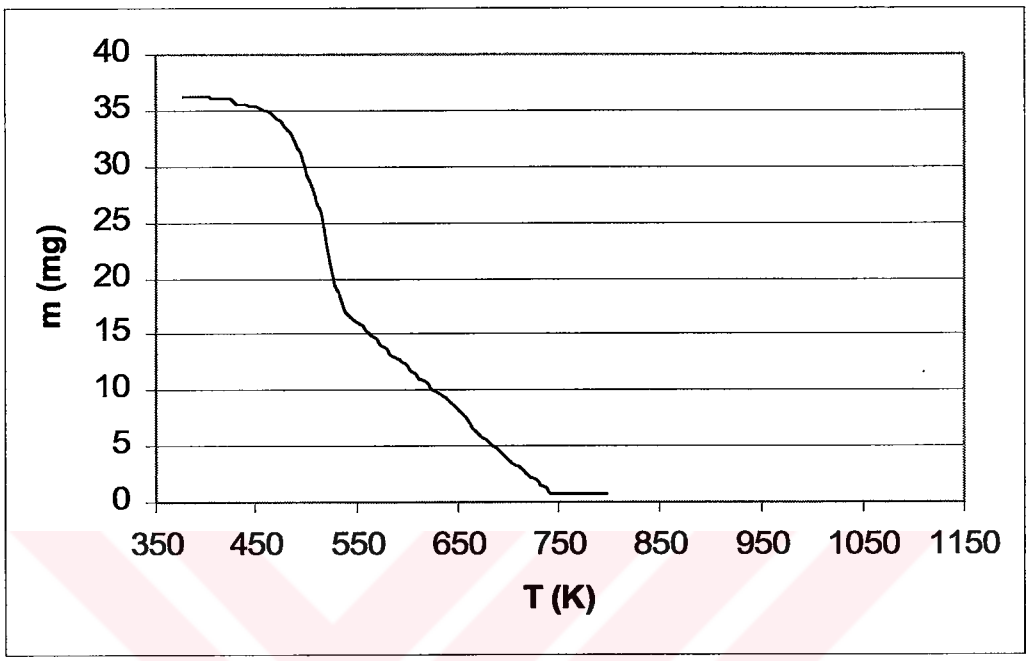

Figure B.17: TG curve of pine conifer with heating rate of 5 K/min

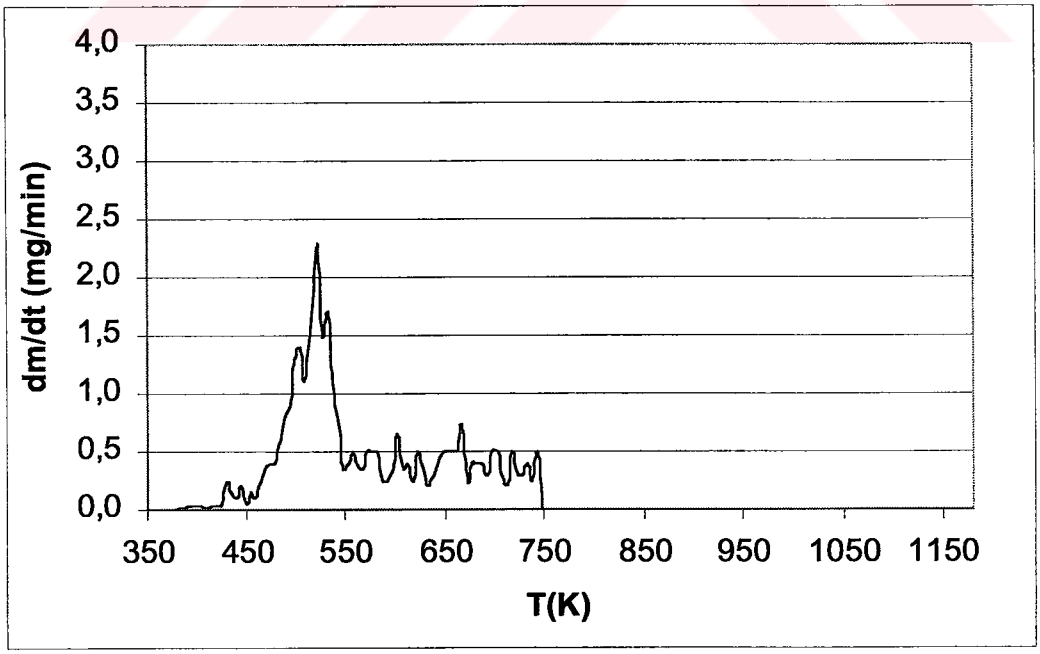

Figure B.18: DTG curve of pine conifer with heating rate of 5 K/min

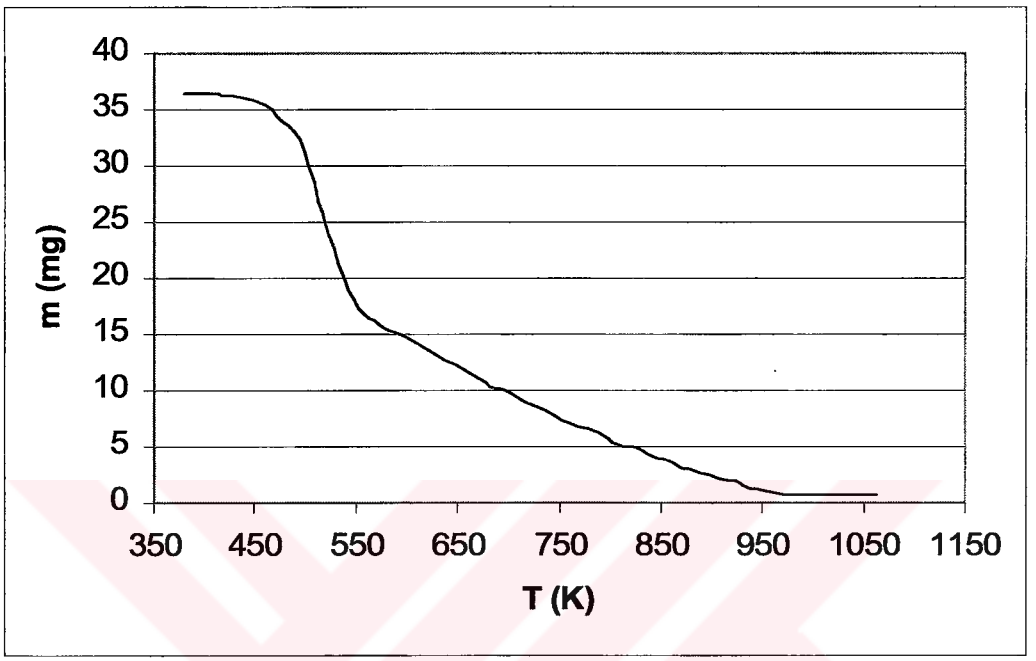

Figure B.19: TG curve of pine conifer with heating rate of 10 K/min

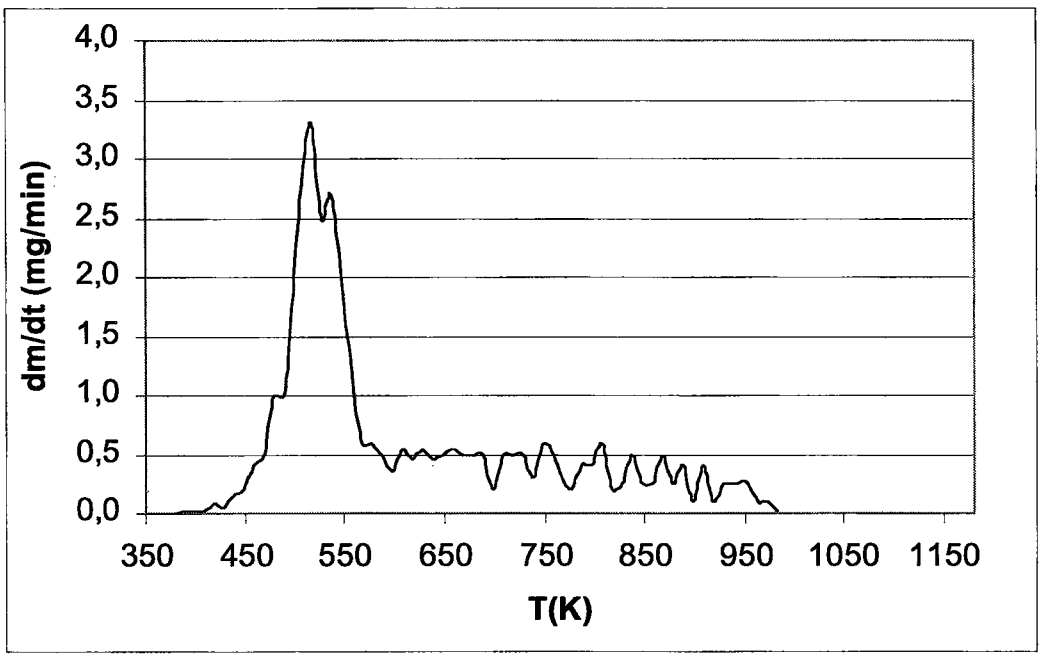

Figure B.20: DTG curve of pine conifer with heating rate of 10 K/min

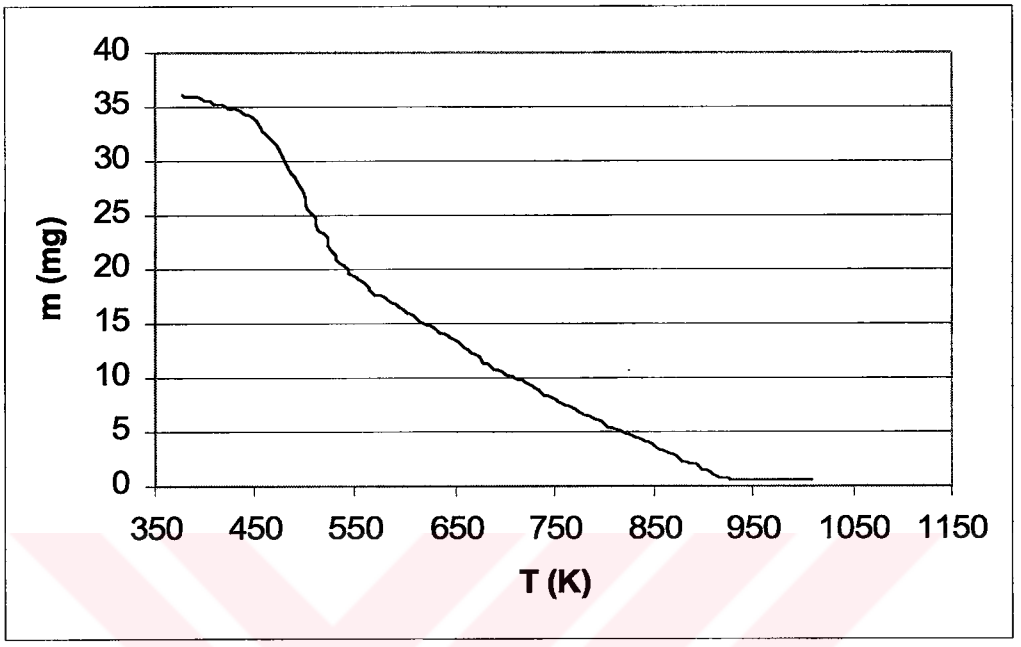

Figure B.21: TG curve of tea residue with heating rate of 5 K/min

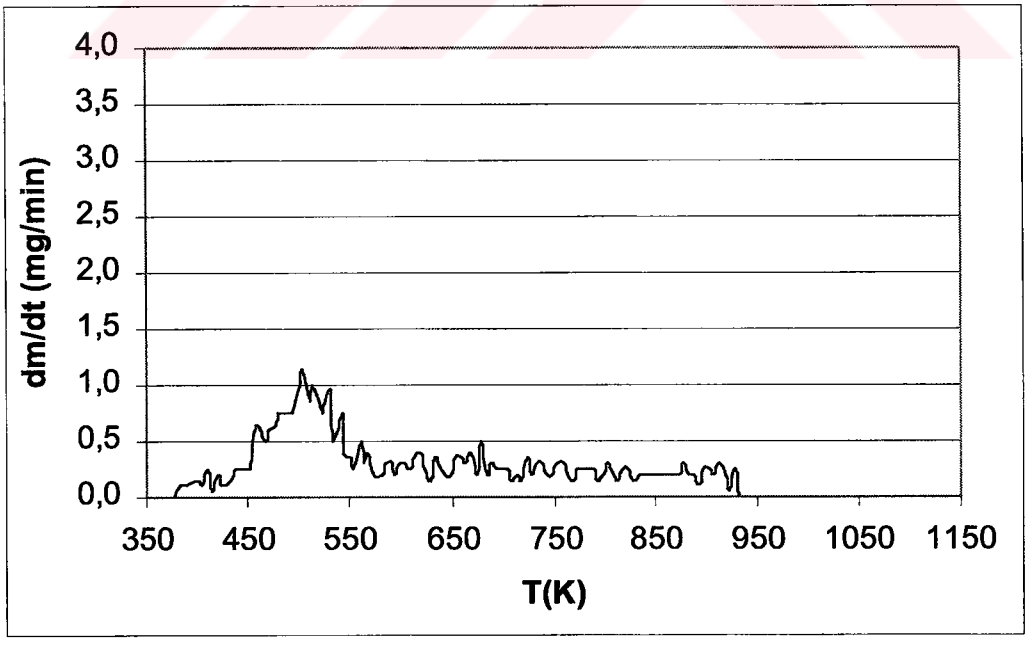

Figure B.22: DTG curve of tea residue with heating rate of 5 K/min

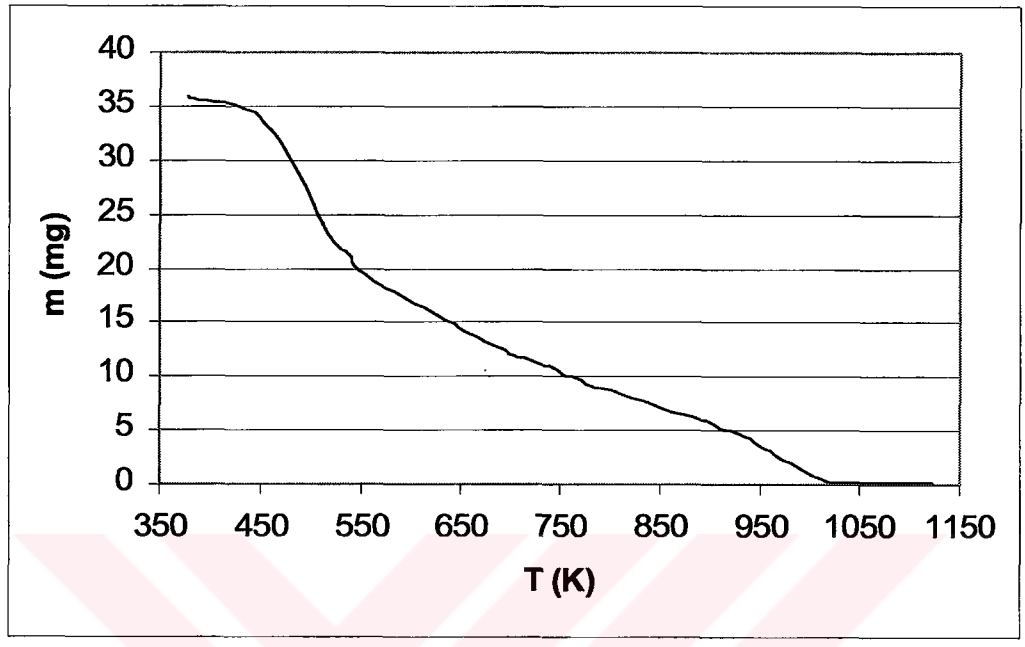

Figure B.23: TG curve of tea residue with heating rate of 10 K/min

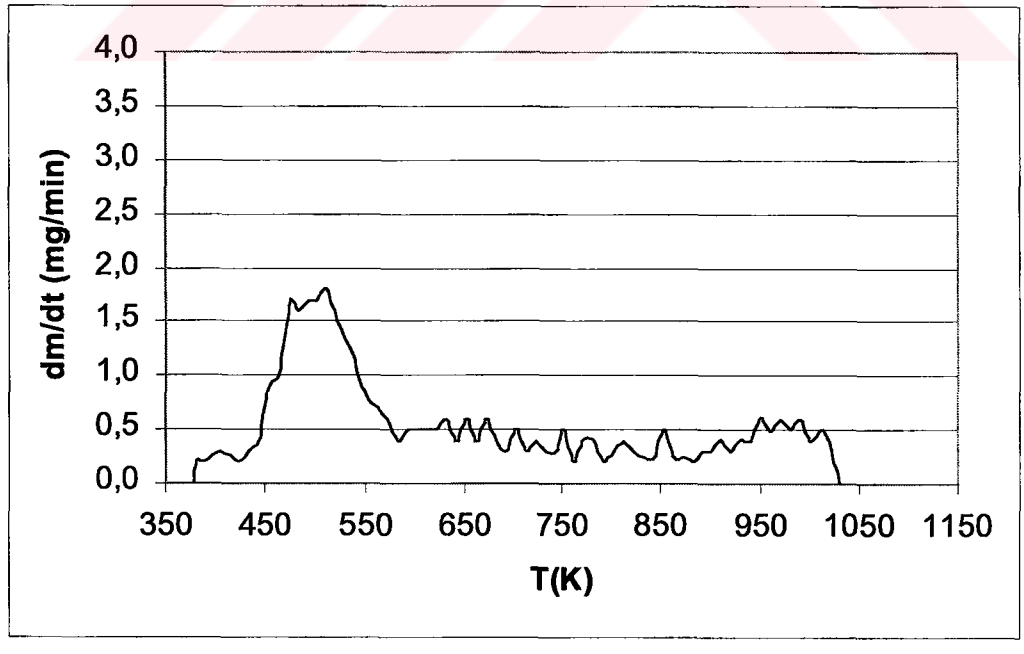

Figure B.24: DTG curve of tea residue with heating rate of 10 K/min

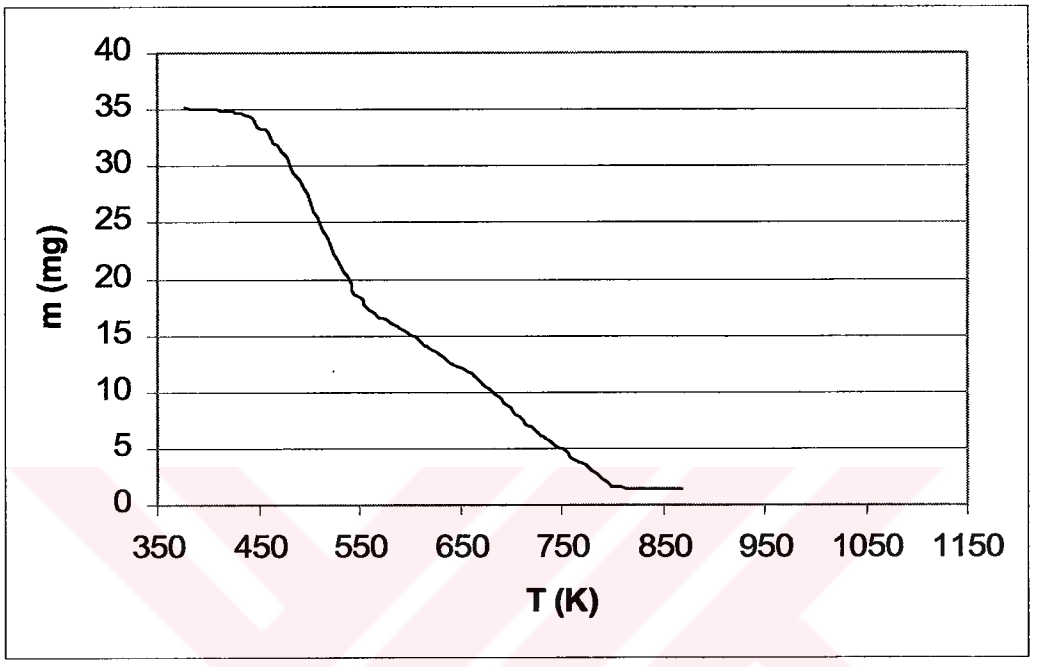

Figure B.25: TG curve of cotton residue with heating rate of 5 K/min

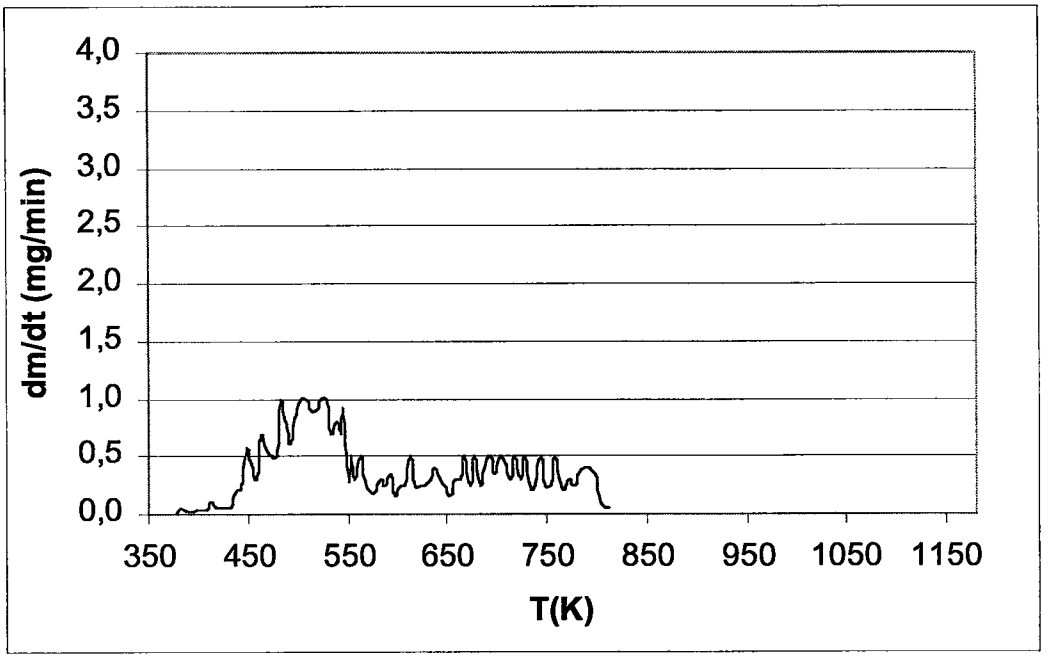

Figure B.26: DTG curve of cotton residue with heating rate of 5 K/min

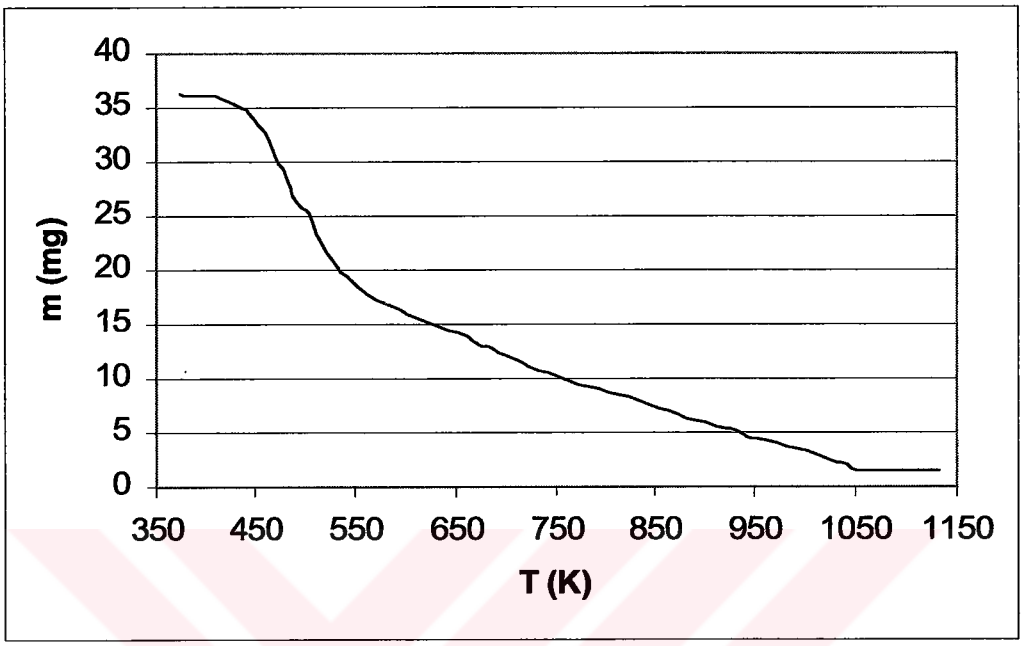

Figure B.27: TG curve of cotton residue with heating rate of 10 K/min

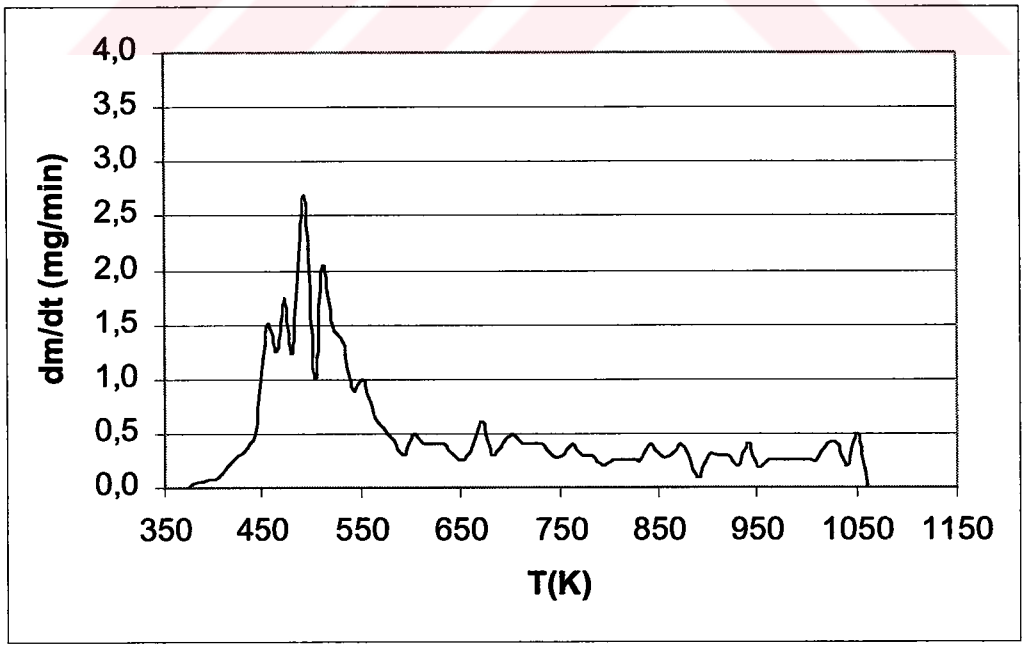

Figure B.28: DTG curve of cotton residue with heating rate of 10 K/min

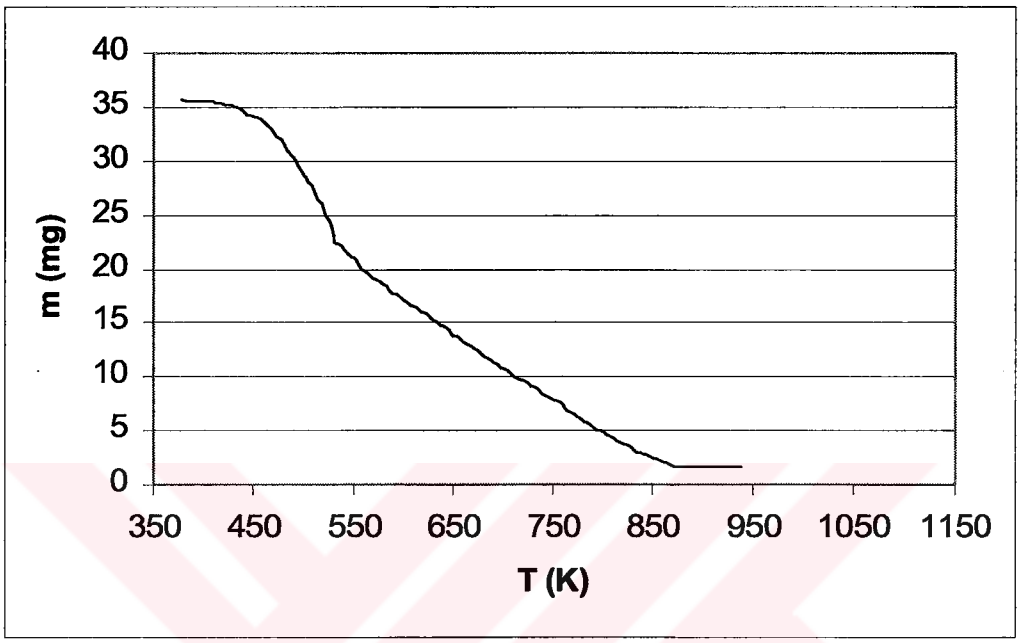

Figure B.29: TG curve of grape seed with heating rate of 5 K/min

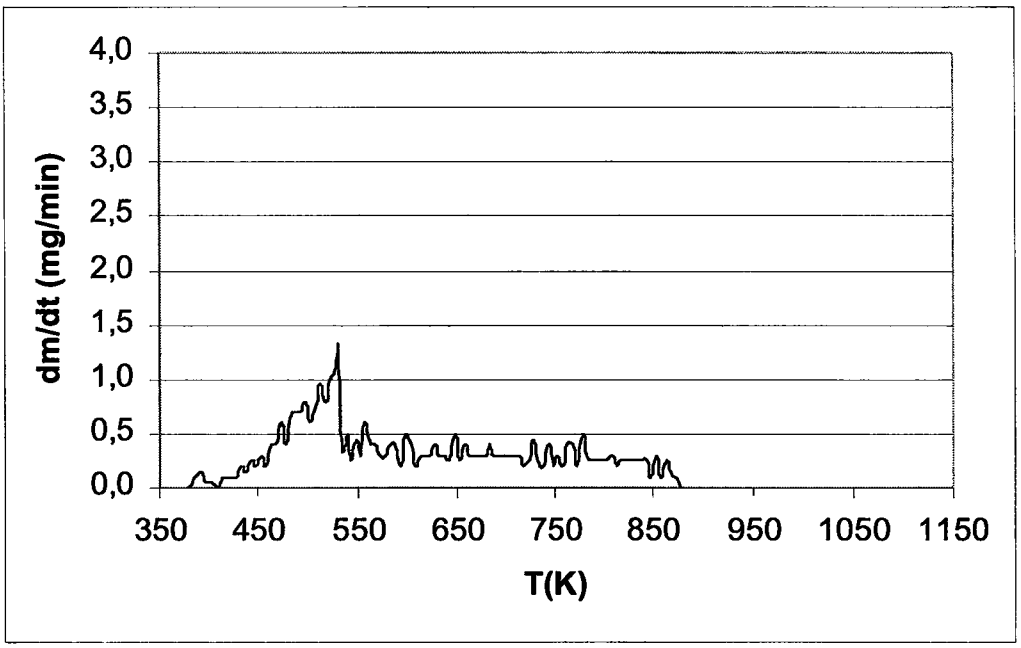

Figure B.30: DTG curve of grape seed with heating rate of 5 K/min

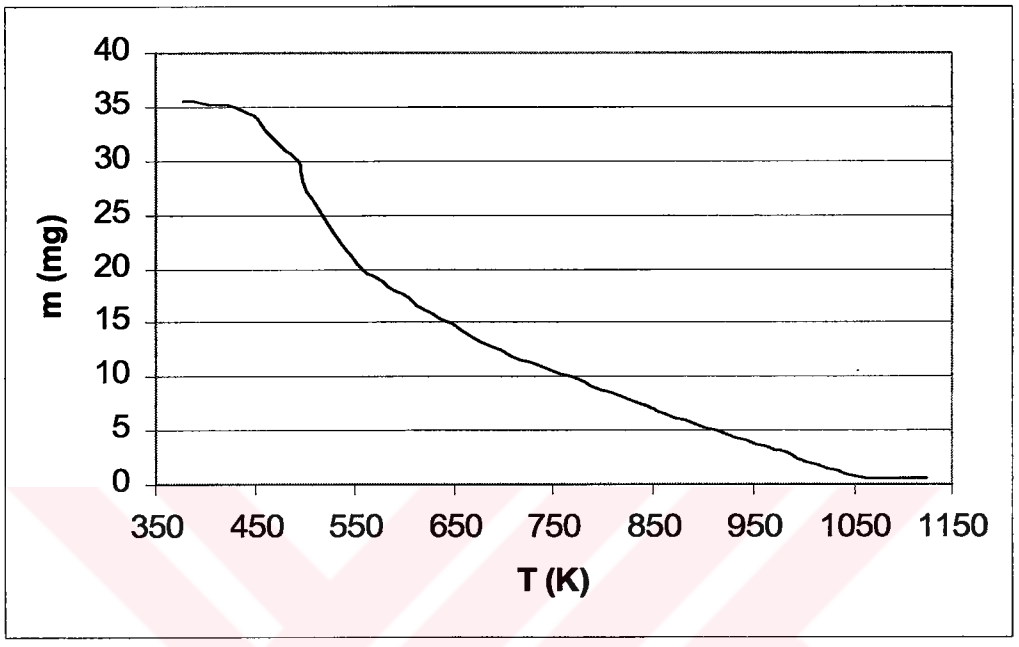

Figure B.31: TG curve of grape seed with heating rate of 10 K/min

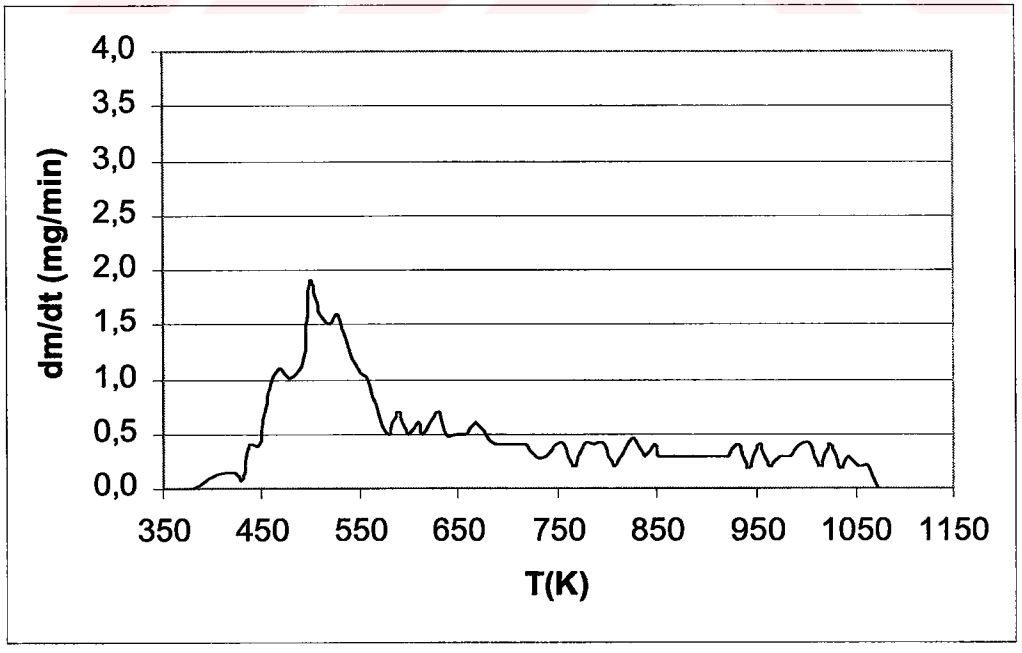

Figure B.32: DTG curve of grape seed with heating rate of 10 K/min

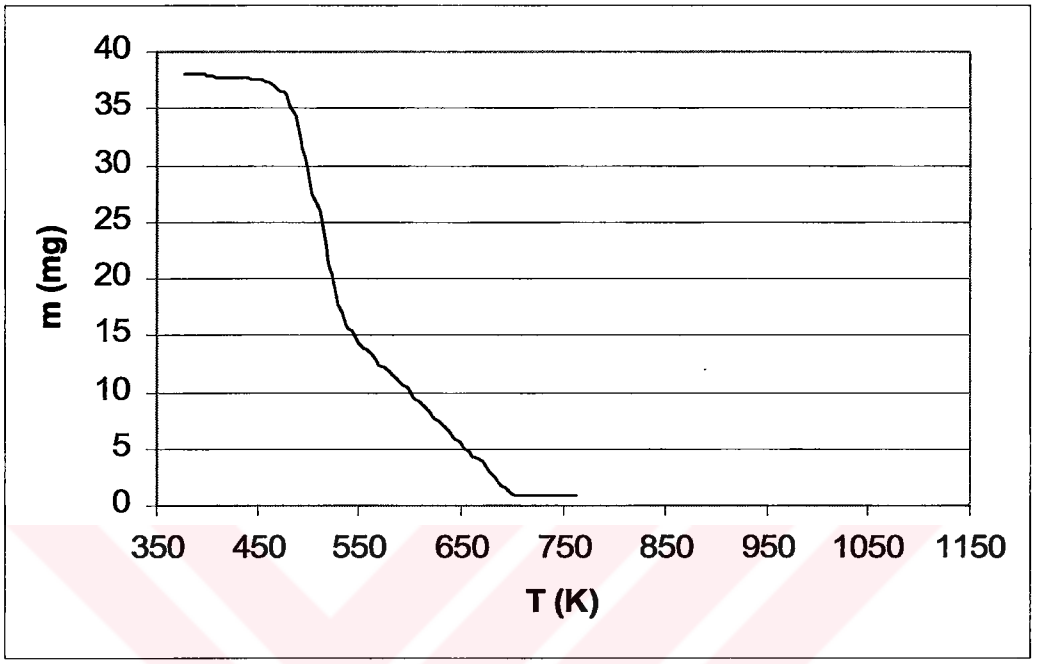

Figure B.33: TG curve of hybrid poplar with heating rate of 5 K/min

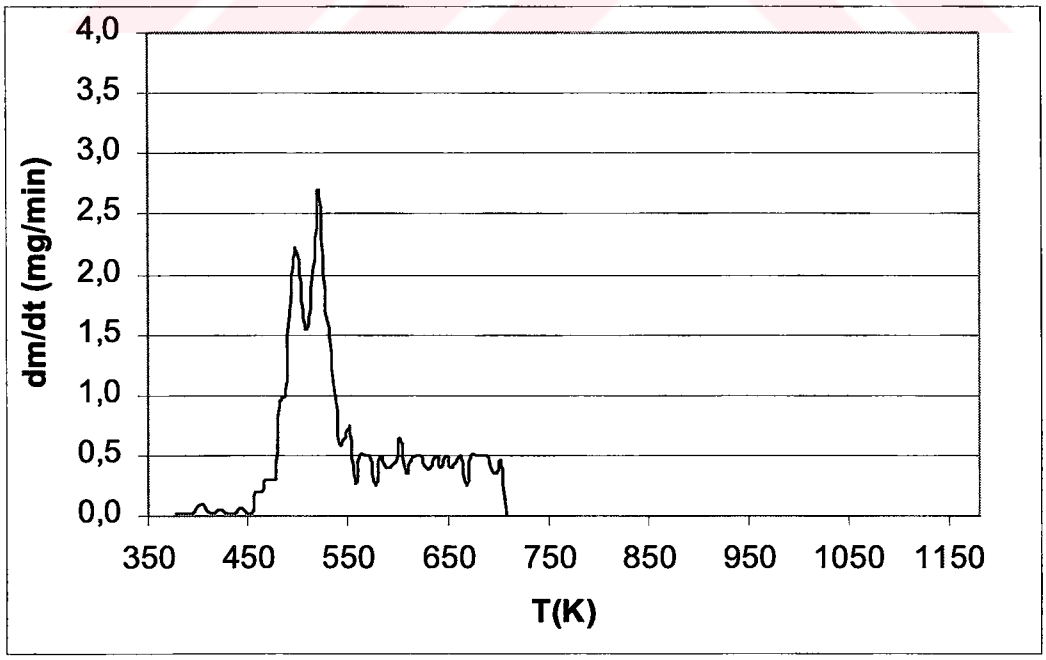

Figure B.34: DTG curve of hybrid poplar with heating rate of 5 K/min

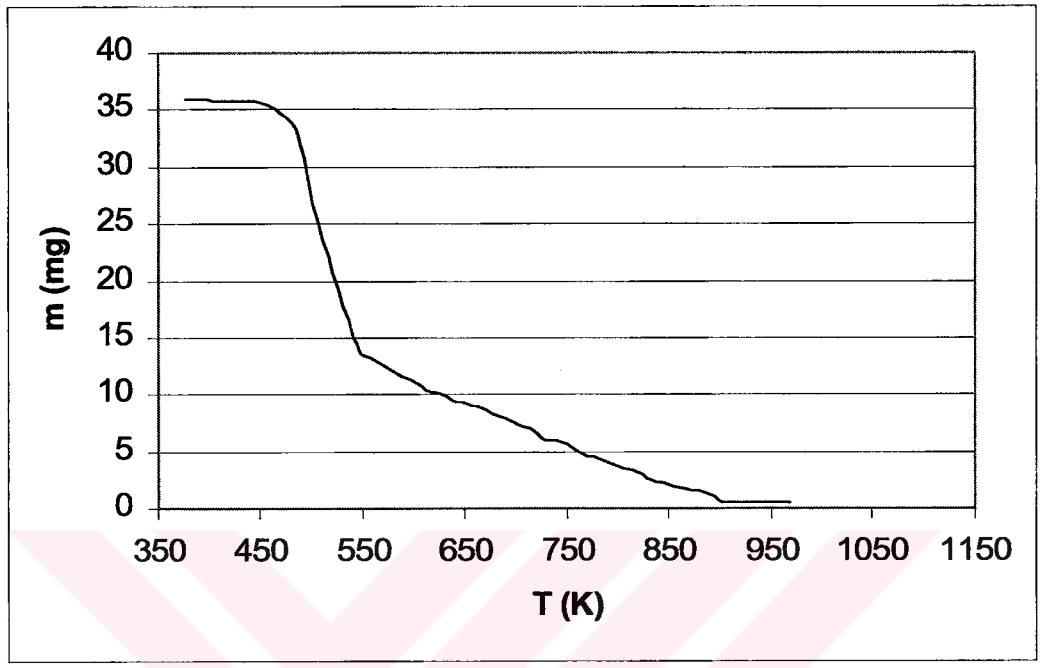

Figure B.35: TG curve of hybrid poplar with heating rate of 10 K/min

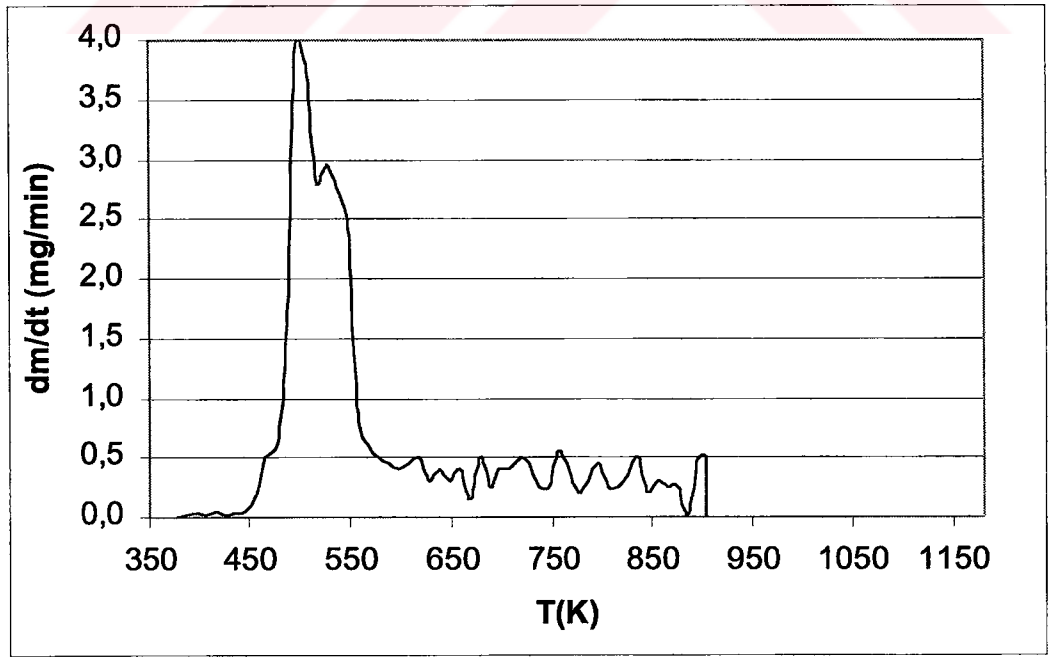

Figure B.36: DTG curve of hybrid poplar with heating rate of 10 K/min

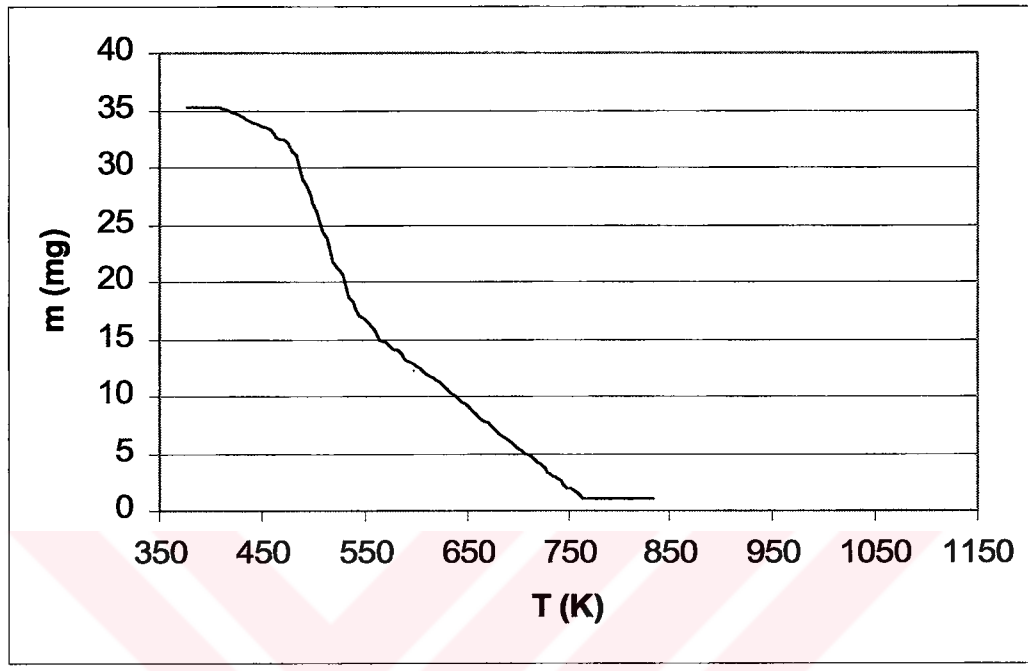

Figure B.37: TG curve of sour cherry stone with heating rate of 5 K/min

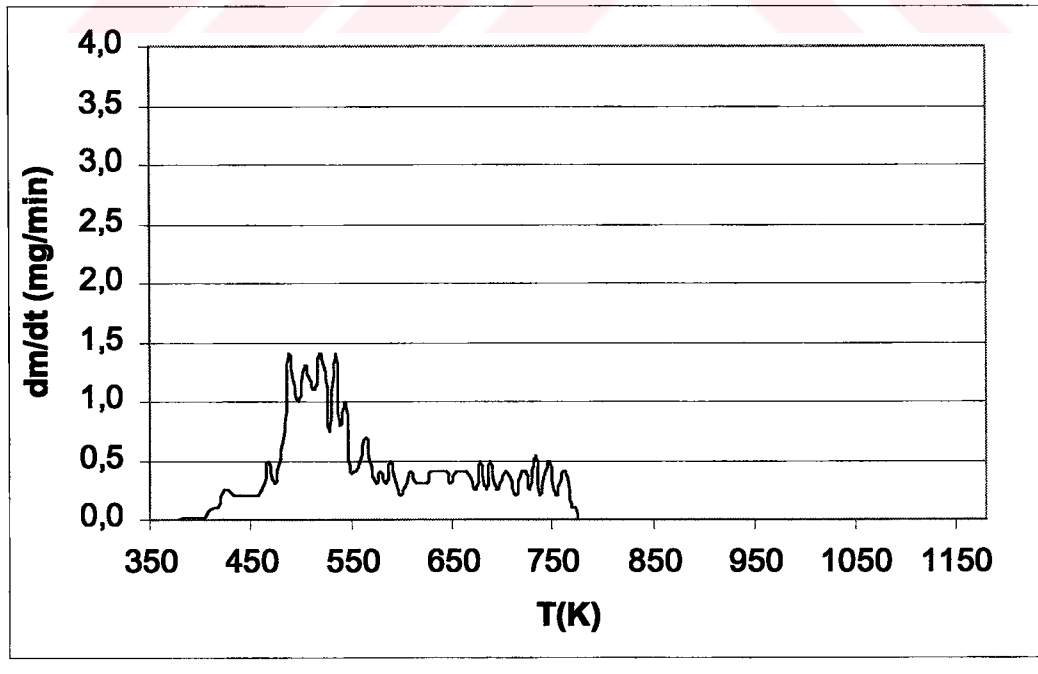

Figure B.38: DTG curve of sour cherry stone with heating rate of 5 K/min

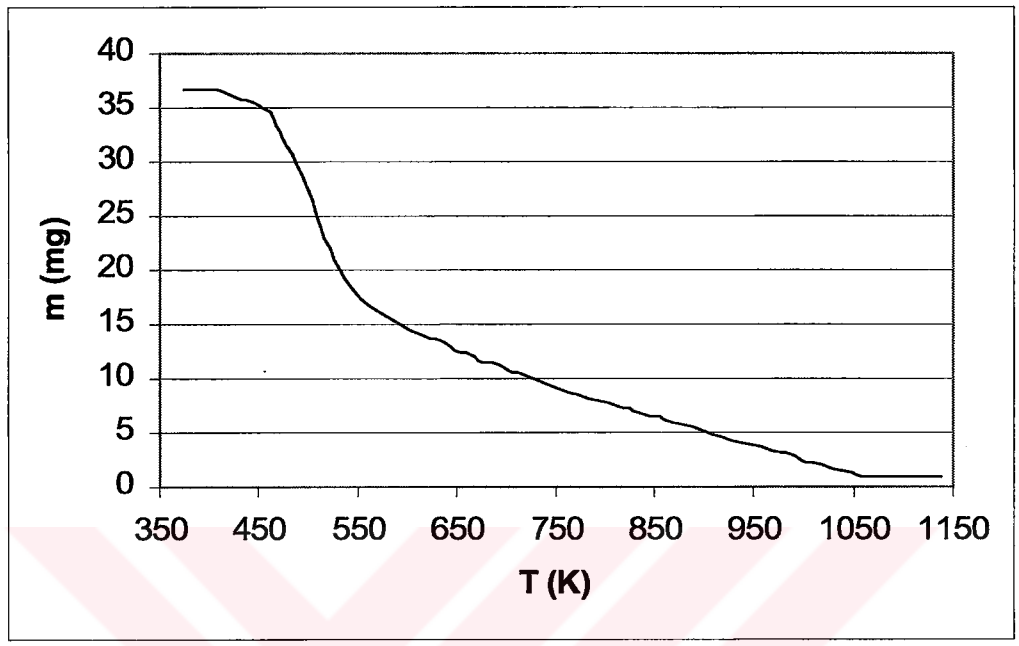

Figure B.39: TG curve of sour cherry stone with heating rate of 10 K/min

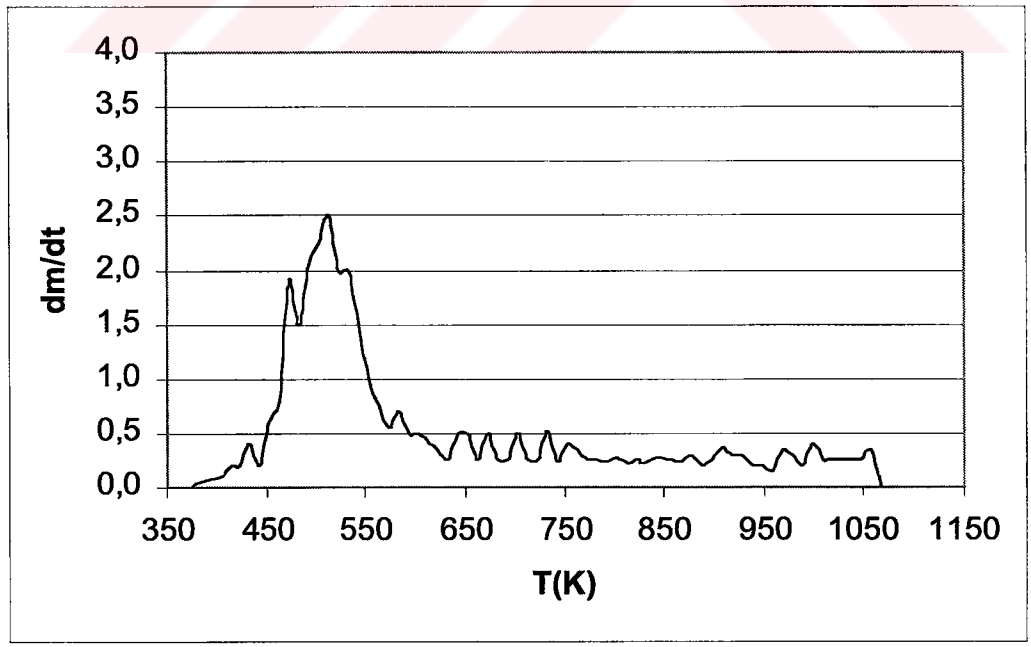

Figure B.40: DTG curve of sour cherry stone with heating rate of 10 K/min

APPENDIX C

Table C.1: Combustion characteristics of biomass samples

Sample	Heating Rate (K/min)	Max. Burning Rate (mg/min)	Temp. of Max. Burning Rate (K)
Olive waste	5	1,65	483
	10	2,30	474
Sunflower seed shell	5	2,10	485
	10	3,60	474
Rapeseed	5	1,25	508
	10	1,90	483
Walnut shell	5	2,30	520
	10	3,60	504
Pine sonifer	5	2,30	523
	10	3,30	518
Tea residue	5	1,15	504
	10	1,80	513
Cotton residue	5	1,00	520
	10	2,70	493
Grapeseed	5	1,30	531
	10	1,90	498
Hybrid poplar	5	2,70	523
	10	4,05	498
Sour cherry stone	5	1,40	515
	10	2,50	513

CURRICULUM VITAE

Born in Istanbul in 1980, Fikriye Seda Yücel got her B.Sc degree in Chemical Engineering in 2003 at Istanbul Technical University Chemistry and Metallurgy Faculty. She is still going on with her M.Sc studies at Energy Science and Technology Program at Institute of Energy at ITU. She has been working as "Quality Control Engineer" at Cam Elyaf Sanayi A.Ş. since August 2005.