OBTAINING HYBRID FUEL BRIQUETTES USING LOCAL BIOMASS AND FOSSIL FUEL RESOURCES

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ABSTRACT

OBTAINING HYBRID FUEL BRIQUETTES USING LOCAL BIOMASS AND FOSSIL FUEL RESOURCES

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This study aims at obtaining a hybrid fossil fuel-biomass fuel by blending olive pomace and lignite in varying amounts (10-50% by weight). The main objective is to combine the positive characteristics of both fuel types to rehabilitate their unfavorable sides that are potential drawbacks against their broader utilization. The suggested hybrid fuel is anticipated to be an effective, environmentally sound, and sustainable fuel alternative. To obtain the hybrid fuel, olive pomace from the Aegean region in Turkey and ROM Tuncbilek lignite characterized with high ash and sulfur content, are used. The project has two major phases: 1. Identification of the fuel characteristics and combustion behavior of hybrid blends; 2. Briquetting of fuel blends to obtain a hybrid fuel form.

In the first phase, the fuel and emission characteristics of the olive pomace and lignite on an individual basis as well as in the form of fuel blends, were determined. The liability of both fuel types and their blends to combustion were also identified. The proximate and ultimate analysis, TG/DTG, DSC, and TG-FTIR work revealed that using olive pomace and lignite in blended form results in significant differences in terms of fuel characteristics, combustion behavior, and combustion liability as compared to the fuels on individual basis. Blending olive pomace and lignite resulted

in reductions in sulfur contents and SO_2 emissions as compared to the lignite alone and the extent of improvement increased as the amount of olive pomace in the blends was increased. This demonstrated that blending high-sulfur lignite with olive pomace could be an effective solution to rehabilitate SO_2 emissions. When the liability to combustion was assessed, it was seen that the activation energy of lignite is approximately 2.5 times less than that of olive pomace. This shows that the liability of lignite to combustion is much higher than that of pomace. Activation energies of fuel blends were also less than olive pomace. This implies that the use of olive pomace with lignite in a hybrid fuel form is more favorable than using olive pomace alone as a fuel, since lignite in the fuel blend can rehabilitate the relatively lower combustion liability of olive pomace. Overall, the results of the investigations on fuel characteristics and combustion behavior revealed that using lignite and olive pomace in a hybrid fuel form can bring notable advantages to both fuel types. The negative aspects related to the use of these two fuels on an individual basis, could be significantly rehabilitated, if they are utilized together in the form of a hybrid fuel. The suggested approach is a novel and a favorable solution that fosters the positive sides of lignite and olive pomace in the body of a new fuel alternative.

In the second phase, which focuses on briquetting, firstly the briquettability of the lignite alone was identified. Lignite briquettes were obtained using 10% (by wt) molasses as a binder. The effects of particle size, water addition, and briquetting pressure on the strength of the briquettes were investigated. In ideal briquetting conditions, the lignite briquettes can show required levels of drop, abrasion, and breakage resistance designated for Type I briquettes in the TS12055 standard. In obtaining hybrid briquettes from olive pomace-lignite blends, firstly the strength characteristics of binderless briquettes were evaluated for several olive pomace related briquetting conditions (such as the amount of olive pomace in blends, particle size of olive pomace, and moisture content). The binderless hybrid briquettes failed to meet the strength conditions for Type I briquettes. Yet, in ideal briquetting conditions they could meet the required abrasion and breakage resistance levels designated for Type

II briquettes, thanks to the limited binding effect of olive pomace. As a last step, olive pomace-lignite blends were briquetted using binding agents to satisfy strength designations for Type I briquettes. The blends were briquetted, firstly, by using only molasses and then by using molasses+lime. The strength properties of the binder-added hybrid briquettes were determined with respect to varying quantities of molasses addition (5-15% by wt.) and lime addition (4-6% by wt.). It was seen that, even with 5% molasses addition, strength requirements for Type I briquettes could be achieved. Obtaining favorable strength features with limited molasses addition was attributed to the binding effect of olive pomace: Pomace in the blends successfully reduced the required binder amount or obtaining fuel briquettes with sufficient strength characteristics. Use of lime as a binder along with molasses could not provide an apparent improvement in the strength of the briquettes. On the other hand, none of the briquetting conditions studied in this project could provide water-resistant briquettes. This is a well-known problem common for most Turkish lignite. To overcome this problem, the hybrid briquettes could be supplied in sealed bags to the market, as suggested in the TS12055 standard.

To conclude, this study showed that utilization of olive pomace and lignite in a hybrid fuel form can lead to several benefits in terms of fuel quality, combustion behavior, and SO_2 emissions. It is very advantageous to stimulate the positive sides of both fuel types while controlling and reducing the negative features of lignite and olive pomace by utilizing these fuels in a hybrid form. This approach is therefore an effective solution towards an extensive, sustainable, and environmentally sound utilization of these fuel types. Proven briquettability of the olive pomace-lignite blends is another important aspect that would contribute to the broader use of the suggested hybrid fuel.

Keywords: Fossil Fuel, Biomass, Lignite, Olive Pomace, Briquetting

ÖZ

YERLİ ENERJİ KAYNAKLARIMIZDAN FOSİL YAKIT-BİYOKÜTLE BAZLI HİBRİT YAKIT BRİKETİ ELDESİ

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Bu çalışmada pirina ile linyitin ağırlıkça çeşitli oranlarda (%10-50) karıştırılmasıyla hibrit bir fosil yakıt-biyokütle enerji kaynağı eldesi hedeflenmiştir. Çalışmanın en önemli amacı her iki yakıtın olumlu özelliklerinin bir araya getirilmesiyle hem pirina hem de linyitin kullanımını olumsuz etkileyen özelliklerin iyileştirilmesini sağlamak, yerel iki enerji kaynağımızdan, yaygın şekilde kullanılabilen, çevreye dost ve sürdürülebilir alternatif bir yakıt formu elde etmektir. Önerilen hibrit yakıtın eldesinde, Ege Bölgesi'nden getirilen pirina ile yüksek kül ve kükürt içerikli tüvenan Tunçbilek linyiti kullanılmıştır. Çalışma iki ana safhadan oluşmaktadır. Bu safhalar; 1-Hibrit karışımların yakıt özelliklerinin ve yanma davranışlarının belirlenmesi; 2-Karışımların hibrit bir yakıt formuna dönüştürülmesi amacıyla briketlenmesidir.

İlk safhada pirina ve linyitin önce ayrı ayrı daha sonra karışım halinde yakıt, yanma, emisyon özellikleri ve yanmaya olan yatkınlıkları belirlenmiştir. Kısa ve elementer analizler, TG/DTG, DSC, ve TG-FTIR çalışmaları sonucunda, pirina ve linyitin bir karışım halinde kullanılmasının, yakıtların tek başlarına kullanılmalarına göre, yakıt özellikleri, yanma davranımları, SO_2 emisyonları ve yanmaya olan yatkınlık bakımından önemli farklılıklar sağladığı belirlenmiştir. Pirina-linyit karışımlarının

kükürt içerikleri ve SO_2 emisyonlarında, tek başına linyit ile karşılaştırıldığında, belirgin iyileşmeler söz konusudur. Hibrit karışımlardaki pirina oranı arttıkça, karışımların S içeriği düşmekte, SO_2 emisyonları azalmaktadır. Bu durum, kükürt içeriği yüksek linyitlerimizin, pirina ile karıştırılmasıyla SO_2 emisyonlarının azaltılmasına yönelik rehabilite edilebileceğini ortaya koymaktadır.

Yanmaya olan yatkınlıklar incelendiğinde linyitin aktivasyon enerjisinin pirinaya göre yaklaşık 2,5 kat düşük olduğu, yani linyitin pirinaya göre, yanmaya çok daha yüksek yatkınlık gösterdiği belirlenmiştir. Hibrit yakıt karışımlarının da aktivasyon enerjisi, tek başına pirinaya göre daha düşük olup karışımlar pirinaya göre yanmaya çok daha yüksek yatkınlık göstermektedirler. Dolayısıyla, pirinanın yakıt olarak tek başına kullanılmasındansa, linyit ile birlikte hibrit formda kullanılmasının çok daha verimli olacağı, çünkü pirinanın yanmaya olan düşük yatkınlığının linyit katkısı ile rehabilite edilebildiği belirlenmiştir. Yakıt ve yanma özelliklerine ilişkin sonuçlar birlikte değerlendirildiğinde linyit ve pirinanın bir hibrit yakıt formunda kullanılması halinde hem linyit hem de pirina için önemli avantajların söz konusu olduğu belirlenmiştir: Her iki yakıtın tek başına kullanılmaları durumunda geçerli olan olumsuzluklar, bu iki yakıtın birlikte kullanımı ile önemli ölçüde rehabilite edilmektedir. Önerilen hibrit yakıt formu, linyit ve pirinanın olumlu özelliklerini öne çıkaran, olumsuz özelliklerini önemli ölçüde ortadan kaldıran yenilikçi ve faydalı bir yaklaşımdır.

İkinci aşamada, yani briketleme çalışmalarında, öncelikle linyitin briketlenebilme davranımı incelenmiş, bağlayıcı olarak ağırlıkça %10 melas katkısı ile linyit briketleri elde edilmiştir. Tane boyutu, su ilavesi ve briketleme yükünün briketlerin dayanım özelliklerine etkileri belirlenmiş olup ideal şartlarda, TS12055 standardında Sınıf 1 briketler için gerekli kırılma, aşınma ve düşme sağlamlıkları sağlanabilmektedir. Hibrit pirina-linyit briketlerinin bağlayıcısız briketlenmesi aşamasında pirinaya ilişkin briketleme parametrelerinin (karışımdaki pirina miktarı, pirina tane boyutu ve nem içeriği) briketlerin dayanım özelliklerine etkileri belirlenmiştir. Çalışmalar sonucunda pirinanın sınırlı bağlayıcı etki gösterdiği ve pirina-linyit karışımlarının bağlayıcısız briketlenebildiği görülmüştür. Fakat Sınıf 1 için gerekli dayanım koşulları sağlanamamakta, ideal briketleme koşullarında, pirinanın gösterdiği sınırlı bağlayıcı etki sayesinde, ancak Sınıf 2 briketler için gereken aşınma sağlamlığı sağlanabilmekte, gerekli kırılma sağlamlığına önemli ölçüde yaklaşılmaktadır. Son aşamada hibrit briketlerin, TSE12055'de Sınıf 1 tipi briketler için geçerli dayanım koşullarını sağlaması amacıyla bağlayıcı ilavesiyle briketleme yapılmıştır. Karışımlar önce melas daha sonra melas+kireç kullanımıyla briketlenmiş, melas (ağırlıkça %5-15) ve kireç miktarlarına (ağırlıkça %4-6) göre, briketlerin dayanım özellikleri belirlenmiştir. %5 melas ilavesinde dahi, Sınıf 1 briketler için gerekli kırılma ve aşınma sağlamlığı tamamen, düşme sağlamlığı çok büyük ölçüde karşılanabilmektedir. %5 melas ilavesinde dahi dayanım özelliklerinin iyi seviyelere gelmesinin, pirinanın -sınırlı da olsa- bağlayıcı etkisinden kaynaklandığı sonucuna varılmıştır. Yani, pirina varlığı, briketleme için gerekli bağlayıcı miktarını azaltabilmektedir. Melas ile birlikte kireç ilavesi ise dayanım özelliklerinde belirgin bir iyileşme sağlayamamaktadır. Öte yandan çalışmada elde edilen briketler hiçbir koşulda, suya dayanım gösterememektedir. Bu sorun linyitlerimizin çoğu için geçerli olup, hibrit briketlerin, TSE12055 standardında belirtildiği üzere kapalı ambalajlar içinde satılması bu duruma çözüm olarak önerilebilir.

Sonuç olarak, pirina ve linyitlerimizin birlikte, hibrit yakıt formunda kullanılmalarının yakıt özellikleri, yanma davranımları ve SO_2 emisyonları bakımından önemli faydalar sağlayabildiği belirlenmiştir. Hibrit kullanım sayesinde, iki yakıtın olumlu özelliklerinin öne çıkması ve olumsuz özelliklerinin rehabilite edilebilmesi çok önemli bir avantaj olup, her iki yakıtın daha yaygın, sürdürülebilir ve çevreye dost şekilde kullanımına yönelik önemli bir çözüme karşılık gelmektedir. Ayrıca, pirina-linyit karışımlarının başarıyla briket formuna dönüştürülebilmiş olması da, önerilen hibrit yakıtın yaygın şekilde kullanılabilmesini sağlayabilecek önemli bir husustur.

Anahtar Kelimeler: Fosil Yakıt, Biyokütle, Linyit, Pirina, Briketleme

To my dear husband

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Abbreviations

ROM	Run-of-mine
OP	Olive Pomace
L	Tunçbilek lignite
Çan	Çanakkale region
CMC	Carboxymethylcellulose
ASTM	American Society for Testing and Materials
TGA	Thermogravimetric Analysis
DTG	Differential Thermogravimetry
DSC	Differential Scanning Calorimetry
EGA	Effluent Gas Analysis
BEPA	Biomass Energy Potential Atlas
XRD	X-Ray Diffraction
FTIR	Fourier Transform Infrared Spectrometer
SI	Shatter Index
WR	Water Resistance
P_{100}	100% of passing product size

Units

%	percentage
kg/cm^2	kilogram/centimeter square
rev/min	revolution/minute
TEP/year	Ton equivalence petroleum/year
kcal/kg	kilocalorie/kilogram
mm	millimeter
°C	Celsius degree
kj/mol	kilojoule/mol
mg/min	milligram/minute
MPa	mega Pascal

LIST OF SYMBOLS

Symbols

$F_1,\ldots,F_n$	% weight loss occurring in the reaction regions
$E_1,\ldots,E_n$	Activation energies of reaction regions
E_{mw}	Cumulative activation Energy
C	Carbon
H	Hydrogen
N	Nitrogen
S	Sulfur
CO_2	Carbon dioxide
CO	Carbon monoxide
SO_2	Sulfur dioxide
H_2O	Water
A	Arrhenius constant
E	Activation energy, kJ/mol
T	Temperature, in K and °C
N	Reaction order
R	Gas constant, 8.314 j/molK
λ	Number of sieve
l_{ave}	Average particle size of sample after shatter test
c_i	Weight percentage of sample oversize of sieve I and passing through the i+1
l	Diameter of briquette
$l_{ave,i}$	Average aperture size of i and i+1
T_s	Average load value of failure of briquettes left in water
T_o	Average load value of failure of original briquettes

CHAPTER 1

INTRODUCTION

Energy is a crucial necessity worldwide. Energy shortage has become a major problem for the developing countries in the world and especially in Turkey. As a result of population growth, industrial development and improvement in the quality of life, reserves as energy sources are rapidly depleting so the use of underground and surface resources became more important. Coal is an important energy source because of the wide variety and the cheaper potential compared to other fuels. With the rapid reduction of reserves, the assessment of low-quality coal and the use of biomass, industrial energy, are aimed at providing the need for energy with briquetting technology. Biomass energy has found great opportunities for being an environmentally friendly and sustainable energy source, providing safe environmental management and targeting development throughout the world. For this reason, utilization of biomass energy has gained importance as an energy source in Turkey (Karayılmazlar et al. 2011).

Briquetting is an appreciable method and also universally accepted to deal with energy shortage. The process of briquetting consists of applying pressure to a mass of fine particles with or without a binder to form a new compact body (Lowry, 1963). In other words, briquetting of coal is the process of converting the powdered coal into a solid, high quality fuel in a mold, pressurized in the form of a cube, cushion, cylinder, or egg shape, by heating under suitable conditions and / or mixing with various additives (Kural , 1988).

Briquetting methods and developments made coal briquettes as an alternative by using the fine particles of coal in the form of a durable, compact, and costly friendly fuel. Recently, coal industry is influenced by the economic and environmental impact of briquetting technology (Altun, 2002). The importance of coal briquetting is variable but the important advantages of coal briquetting are increasing the calorific value of the coal, avoiding the coal dusts mix into the atmosphere through chimneys and pipes to decrease air pollution, preventing dust formation and loss of fine coals as dust and decreasing the self-combustion of stockpiles. Consequently, production of coal briquettes is a very important concept based on the characteristics of coal. In recent years, many researches are studied to improve the briquetting of coal.

CHAPTER 2

OBJECTIVES OF THE STUDY

The objective of this work is obtaining a hybrid biomass-lignite energy source alternative by briquetting olive pomace, an important biomass potential in Turkey, and low and medium quality lignite. The main goal is to produce, from the two domestic energy source potentials of Turkey, a sustainable energy resource alternative that is suitable for more extensive utilization through rehabilitating the negative features of lignite by the high calorific value, low sulfur, and ash content of olive pomace. Another purpose of this study is determining whether olive pomace could be evaluated as an alternative organic binder in briquetting processes. The most important objective of this study is to determine the opportunity to evaluate two important and entirely domestic energy resources in the form an environmentally friendly, relatively clean and sustainable fuel by briquetting technique. Olive pomace is mostly considered as a waste and constitutes a major environmental issue. In fact, olive pomace is a significant biomass and renewable energy alternative for Turkey, being an organic material distinguished with a high calorific value and low ash and sulfur contents (Akın, n.d.) However, its utilization as an energy source remains quite limited, inefficient, and this important potential cannot be fully converted to an economic value. Besides, the domestic lignite sources in Turkey are generally characterized as low rank, young age lignite with low to medium calorific values, relatively high sulfur and ash contents. Such negative features constitute an obstacle against clean, effective and extensive, use of our lignite resources.

CHAPTER 3

LITERATURE REVIEW

3.1. Coal and Briquetting of Coal

Coal is a sedimentary rock of fossil origin and one of the most important of the energy sources. It is composed of macerals, microscopic components, or lithotypes, macroscopic components, as an organic part and water and mineral matter as an inorganic part. It is divided into main types of peat, the first phase of coalification, lignite, hard coal and anthracite; therefore, it has a variety of physical and chemical characteristics. Physical and chemical properties of coal are used for the identification of coal, determination of coal quality and potential usage areas.

Coal mainly composed of plants is defined as a combustible solid, organoclastic, and sedimentary rock. The composition of each coal makes up the nature of organic and inorganic components and degree of diagenesis, formation of rocks from sediments (Karayiğit et al., 1998).

Rocks that contain sufficient amounts of flammable organic compounds, which can be used naturally or as fuel after some changes, are called “Mineral Fuels”. Coal, a mineral fuel, is described as an organic rock. It consists of organic, inorganic materials, and moisture. During the coalification, the physical and chemical changes lasted for thousands and even millions of years. In this process, considering the plant species that make up the bed and environmental conditions that are very different, the coal beds of different structure will be formed (Ateşok, 2014).

Coal is a clean fossil fuel that can be obtained with low cost. Coal in Turkey was found for the first time in the village of Kestaneci in Black Sea in 1829 (Parlak, 2010).

Coal, a rock of fossil origin, plays an important role in the development of mankind. Even though other fuels partly take the place of coal, coal which has the highest amount of reserves, will be in the service of mankind for many years. In recent years, the increase in the use of alternative fossil fuels such as petroleum and natural gas has also affected the environment negatively. Therefore, coal is used more commonly all over the world not only in large amounts but also in a cost effective way.

Briquetting is one of the most common methods of fine particle agglomeration. Coal briquetting is a process that is converting of very fine coal particles into a solid that is durable and high quality fuel with pressing in a mold such as cube, cushion, cylinder, or egg shape by heating under suitable conditions and/or mixing with variable additives (Beker et al., 1998).

Scientifically, there are two main purposes of coal briquetting. The first one is to utilize powder coal with sufficient thermal value. The second one is that coal which is difficult to burn due to its high water content is converted into a high thermal value fuel by briquetting and increasing the thermal value by drying. Consequently, lignite with friable, becoming dust very quickly, high moisture content is converted into a high calorific value and a durable fuel even semi-bituminous and bituminous coals are utilized as an alternative fuel. The main advantages of briquetting of coals are;

- Preventing the dust formation and loss of fine coals as dust,
- Preventing the falling coal particles under the grizzly during combustion,
- Avoiding the coal dusts mix into the atmosphere through pipes and chimneys to decrease the air pollution,
- Decreasing the self-combustion of stockpiles,
- Increasing the calorific value of the coal by drying process,
- Decreasing the cost of transportation and deposition by a considerable reduction in coal volume,
- Providing the required size available for usage.

Several economic and environmental impacts on today's coal industry will encourage a trend towards the briquetting process especially in developing countries.

3.1.1. Historical Review of Coal Briquetting

3.1.1.1. Briquetting in the World

Briquette production has been started about 150 years ago in Europe to utilize the dust and fine particles of lignite. In the countries with large coal deposits, production of briquette has developed very rapidly. In 1842, the first briquetting factory has been established in France, St. Etienne. This factory has been followed by similar plants in New Castle, England and Wiesche, Germany. Thanks to the improvements in technology, lignite briquettes have been used as a fuel for indoor heating. In 1848, firstly, a briquetting patent has been taken in USA by William Easby. In 1924, the coal briquette production has begun in Australia and reached an important production potential (Beker et al., 1998).

After the entrance of petroleum and natural gas to the world fuel market, almost all countries began to utilize these sources. As a result of this, briquette production decreased dramatically so also decreased in coal mining. In the mid 1900's, Germany has been the leading producer with a capacity of approximately 68 million tons briquettes. Briquette production still continues in Germany, Russia, Poland, Bulgaria, China, Southern Korea, Australia, and India (Kural, 1988).

3.1.1.2. Briquetting in Turkey

The first important coal briquetting plant in Turkey has been established in Zonguldak in 1939. The object of this plant was to produce briquettes with tar from washed fine coal particles of 0-0.5 mm size. This plant, which has been complemented with a coke-making unit, has reached its highest production with an amount of 134,000 tons in 1960. However, the activity has been permanently ended in 1974. The Kırklareli-Vize briquette factory, with an annual capacity of 150,000 tons, has been established in

1983 with the aim of briquetting the Çan region lignite. However, problems with binders and grinding of hard lignite have resulted in increasing cost. In addition, due to the excess of technological problems and incorrect pricing policy, this modern establishment ended production in 1985 (Kural, 1988).

There are currently briquette facilities operating for regional and different purposes. Ankara and Erzurum/Oltu that use pitch as an additive and are low-capacity factories. In addition to these factories, there is also private factory in Çorum (Kural et al., 1985).

In course of time, many plants of different production capacity continued studies for the briquetting of their fines. As a result of encouraging briquette production, low capacity briquettes are sometimes produced by private sector in the settlement centers such as İstanbul, Çorum, Muğla, Amasya-Merzifon, and Konya (Hiçyılmaz et al., 2004).

After then, some other briquetting plants started activity in Ankara, Erzurum, İstanbul, and some other cities. A new briquetting plant has been opened to service by BELKO in Ankara in 1986 to produce briquettes from the fine coal particles of the South African coals. In this briquetting facility belonging to Turkish Coal Enterprises Institution, coke dust and mixture of coal dust residual from imported coal brought to Ankara were briquetted adding tar as a binder (Ateşok et al., 2014).

Another facility to briquette facilities coal dust was built in Merzifon, Amasya. Cemre Briquette Plant was built in 1994 in Gebze Dilovası where briquetting is performed with powdered coal imported from Siberia using with molasses and limestone binders.

3.2. Briquetting Theories

In the briquetting of coal, the physical properties of coal and chemistry of its surface are important; in the carbonizing of briquetting, and in the briquetting of hot coal, it is essential to have knowledge of both the physical and chemical changes that take place when the coal is heated (Lowry, 1963).

Many researchers such as Scheithavser claimed that the stability of the briquettes depends on the attachment forces of the bitums. On the other hand, Kegel thought that this is based on the water molecules located in the pores of the particles. Fritsch, who took this theory of Kegel, developed this study. However, Agde said that briquetting is completely related with the structure of the coal particles (Elliot, 1981).

There are studies that have been carried out in order to improve the interpretation and technique of the factors affecting the briquetting process, theoretically. In addition to these studies, various theories about the physical structure of the coal have been proposed (Bayar et al., 2012).

Although there is the great number of researchers, none of the theories have been capable of explaining the briquetting alone. New studies always lead to findings, parameters and variations according to the source, structure and characteristics of the coal. The most important theories about briquetting are;

1. Bitum Theory
2. Capillary Theory
3. Molecular Energy Theory

Bitum Theory: This theory is one of the first theories attempting to explain briquetting. Preipig, Wendtland, Sxheithaver, and Hurte are the scientists who contributed in the formation and development of this theory which states that the bitums approximately 4-10% inside the coal and cover the surface of the coal particles and the briquette, the amount of bitum inside the coal should be at least 2-6% and at most 13-14%. The parameters in the briquetting of the coal by means of the bitums inside are; the water content of the coal, particle size, briquetting temperature, and pressure applied (Kural, 1988).

Capillary Theory: This theory explains that the briquetting process is by the exit of the water molecules from the capillaries of the coal under the effect of high pressure and strengthens the combination of them with the water molecules located in the other capillaries and form a water film around the coal particles. Thus, the natural water content of the lignite acts like a binding agent. The higher water contents of the lignite, the larger the capillaries of it. According to this theory, coal containing very high or very low moisture content are not practically briquetted.

Molecular Energy Theory: The relationship between the coal particles and the molecular energy has been investigated by Kegel. According to Kegel, since the surface area of the particles increase as the particle size is reduced, the molecular energy increases. Consequently, the finer the lignite particles, the stronger the briquettes produced. According to this theory, when binderless briquetting is preferred, it is essential to use fine particle sizes. To be able to utilize the molecular forces, the particles should be kept as near as possible to each other and this is only achieved at high pressure levels.

3.3. Briquetting with and without Binder

The method of briquetting with binder is the briquetting of hard coal using an appropriate binder. This method was first applied in China with powdered coal by adding bentonite as a binding material. In Central Europe countries with rich peat and soft lignite deposits, it is possible to produce briquettes with sufficient strength without using of additives. However, old and hard coal can only be briquetted with the help of a binder. Also, in Turkey, the vast majority of lignite with high mineral content can be briquetted using binders. Since bituminous and semi bituminous coals are moderately hard coal type and it is needed to use several binders in briquetting process. When these types of coal are briquetted without binder, briquettes are dispersed easily when they come into contact with water or when they are in humid environment (Bayar et al., 2012).

Also, according to Lowry (1963), the function of the binder has to be an adhesive and it must be wet and cover the surfaces to be stuck together.

Turkish lignite have a fragile character and as a result, coal is pulverized by 30-40% during the production, preparation, transportation, and storage. Especially, in long term storage, with the effect of dust, moisture loss, and oxidation, this rate reaches up to 60% (Parlak, 2010).

In this briquetting method, the type of binders and the rate of incorporation into the coal are the most important parameters affecting the briquette strength. Also, the optimum amount of binder to be used in briquetting must be determined. There are some of the factors that should be considered in the choice of binders. Some of them are that;

- The binder should have excellent binding ability.
- It should be able to be distributed homogeneously and easily on the surface of the coal particles.
- It should have a similar chemical structure to the coal.
- It should have considerable agglomeration characteristics.
- It should hold the briquette together satisfactorily in the fire.
- It should be combustible at low temperatures.
- It should have a high calorific value.
- It should not be harmful for human health and should be environment friendly during the combustion.
- It should be cheap to make the manufacture of briquettes profitable and scalable

The binders can be classified in two main groups as organic and inorganic.

Organic Binders: Since the beginning of the briquetting process, the organic binders have always found a great application in the industry. The most important organic binders used in the industry are;

- Carboxymethyl cellulose (CMC),
- Pitch,

- Petroleum residues (especially Asphalts and Tar),
- Sulphide liquor,
- Molasses, and
- Starch.

Most of the organic binders soften with increasing temperature and this decreases the strength of the produced briquettes. These binders should have sufficient liquidity to coat the surface of the coal particles. Tar, pitch, and asphalts are hydrophobic whereas starch, sulphide liquor and molasses are hydrophilic substances. When hydrophilic substances are used, the produced briquettes should be dried to achieve the required strength. Although the hydrophobic organic binders always let the briquettes get the necessary strength and resistivity against water, they cause additional air pollution since they produce smoke during combustion. As a result, the tendency is towards the usage of molasses, sulphide liquor, and similar type of organic binders instead of petroleum products or pitch in the last years. Furthermore, usage of molasses and sulphide liquor is cost effective when compared with the petroleum based binders (Kural et al., 1985).

Sulphide liquor, tar, and molasses binders were used with Konya-Ermenek coals and it was stated that successful results could be obtained with samples below 2 mm (Buzkan, 1998).

It was stated that a mixture of Kaya-Denizli lignite and import coal dusts can be used to produce briquettes which are not resistant to water but have good mechanical strength using molasses and as a result of the laboratory test, it was stated that the ideal molasses amount was 12%. The use of molasses as a binder in briquettes has to be the necessity of bagging of briquettes because it causes low resistance to water (Deniz et al., 2001).

Inorganic Binders: Inorganic binders are more economic when compared with the organic ones but they are easily affected by weather conditions. The most important inorganic binders are;

- Cement,
- Clay,
- Lime,
- Magnesium oxide,
- Alkali silicates.

Of these, cement, clay, and lime are not soluble whereas alkali silicates are water soluble. Water is vital in case of inorganic binder usage and the binding is based on chemical reactions. Although sodium silicates and cement binder are suitable for briquette durable in water, they increase the ash amount of briquettes at the end of combustion so briquette producers are not interested in this type of binders. The higher the ash content, the harder the usage of this type of binders.

Many researchers have carried out research using various binders in coal briquetting. However, nearly none of the binders alone gave the sufficient results. Since the organic and inorganic binders have oppositely characterized disadvantages, a popular application is the usage of those as supplements. In other words, the combination of organic and inorganic binders is utilized successfully. Among these, molasses+lime, starch+lime, coal-tar-pitch+lime and asphalt+clay have found applications in the industry and proved to be effective.

Briquettes of sufficient strength were obtained by using 6% lime and 16% molasses amount in Çorum region briquetting facilities. However, due to the use of lime, the ash content was increased and it was found that they are not enough water resistant (Acarkan et al., 1994).

Beker and Küçükbayrak (1996) carried out research with that İstanbul-Kemerburgaz lignite samples that were briquetted with and without binders, asphaltite and molasses. Experiments were performed to determine the effects of different moisture contents, different briqeuetting load on impact resistance, and compressive strength of the briquettes obtained with and without binders. Results showed that the maximum shatter index was observed as 8% and 12% of moisture content at 150 MPa and 200

MPa. Briquettes of Kemerburgaz lignite without binders were not water resistant. In addition, water resistance of briquettes using with molasses was much higher value than water resistance of briquettes using asphaltite. In other words, increase in addition rate of molasses increases the water resistance of briquettes. Comparing all these results, it is concluded that Kemerburgaz lignite should not be briquetted without binder material and molasses is an efficient binder for briquetting of Kemerburgaz lignite successfully in terms of strength properties (Beker et al., 1996).

İstanbul-Yeniköy region coal, fine semicokes as domestic fuel, was briquetted with molasses and lime at different ratios. As a result of the experiments, the best strength results were obtained using 10-12% of molasses amount. Also, addition of molasses increases the water resistance. As the molasses + tar ratio increases, shatter index of the briquettes increase. The strength of the briquettes increases by adding 3% of lime. The best results of production of briquetting are 30 tons of briquetting pressure, 12% of molasses + 5% of tar, and 3% of lime (Asmatülıp, 1996).

Low-quality Afşin-Elbistan lignite was blended with high quality Siberian bituminous coal and optimum conditions for briquetting were achieved for these blends with and without binders. In the mixture; molasses, sunflower shell and sawdust were used at different ratios as binders. Low-quality lignite and high-rank coal were briquetted in order to produce a compact, high quality, and stable fuel. In the study, it was concluded out that the mechanical stability of blends of these two coal samples was low. These blends were briquetted using additives such as molasses, sunflower shell, and sawdust as binders in order to improve the mechanical strength of briquettes. High-quality Siberian bituminous coal should be briquetted with binder. Thus, addition of hard-quality coal to soft lignite decreased shatter index and compressive index of briquettes. Shatter index and compressive strength of the briquettes increased with molasses addition rate from 7% to 15%. In addition, briquettes cannot maintain the integrity disperse in water after 20 min of immersion of water. As a result of the study, soft Afşin-Elbistan lignite and high rank bituminous coal can be briqeutted using molasses and sawdust in order to achieve required strength values (Beker et al., 1998).

Kütahya-Seyitömer Turkish lignite was briquetted with biomass samples such as molasses, olive refuse, paper mill waste, and others. The mechanical strength of the briquettes produced from Kütahya - Seyitömer lignite can be improved by adding some biomass samples. Biomass may have a binding ability blending with hard coal. This study pointed out that mechanical durability, shatter index, and compressive strength, of briquettes can be improved with adding biomass samples (Yaman et al., 2001). Water resistance of the briquettes can be improved by adding olive refuse. Of the biomass samples, olive refuse and paper mill waste can be used in the production of durable fuel briquettes (Yaman et al., 2000).

Briquetting without binder is more economic and easier than using with binders. Main idea of this type of briquetting is pressing of coals with optimum moisture. In order to briquette the coal without binders, the coal should be soft, during the briquetting process and have as possible as homogeneous structure. Since the Çanakkale-Çan lignite are hard lignite group, briquettes with binders could not obtained as durable briquettes (Deniz et al., 2002).

Özbayoğlu et al. (2003) studied the influences of some parameters on the mechanical strengths of briquettes. Merzifon-Yeniçeltek washed coal fines were briquetted with molasses and lime combinations. Laboratory tests showed that these coal fines can be successfully briquetted with binders of milk of lime and molasses. These blends satisfy the required strength values in TS120555 standard (Özbayoğlu et al.,2003).

According to Hiçyılmaz and Altun (2004), the briquettes obtained with the combination of 10% molasses, 15% limes, and 10% water gave the best results from the view of both mechanical resistance properties and combustible sulfur amount with SO_2 emission (Hiçyılmaz et al., 2004).

Moreover, it is seen that in the literature, for the effect of the presence of molasses on impact resistance, the mixture of carbon brown seaweed from Bosphorus with 2% by weight addition of molasses did not give appropriate results but when addition rate of molasses was increased, the strength properties of briquettes were achieved effectively. In addition to that, with 5% of molasses addition, impact resistance reached the highest amount of the experiments. When we look at the results of the production of biobriquettes from carbonized brown seaweed in terms of compressive strength, the required values of compressive strength described in TS12055 standard, 130 kg/cm^2 for Type I and 100 kg/cm^2 for Type II briquettes, were provided sufficiently. This means that biobriquettes using carbonized brown seaweed with sufficient amount of molasses were highly durable in terms of compressive strength (Haykiri-Acma et al., 2013).

Molasses as an additional binder is utilized to strengthen the briquettes strength of dried briquettes. Many different kinds of binders were studied and finally it was found that molasses as a cheap binder can improve the briquettes strength. From the results of briquetting molasses with coal, molasses can significantly improve the strength of dried briquettes. In addition, when molasses addition was increased, compressive strength and impact resistance of briquettes were enhanced (Zhong, 2017 and Benk et al., 2011).

3.4. Briquetting Characteristics

3.4.1. Analysis of Coal

Analyses of coal are proximate analysis, ultimate analysis and thermal value determination. Proximate analysis of coal determines moisture, volatile matter, ash percentages, and fixed carbon. This analysis is carried out according to ASTM (American Society for Testing and Materials) D3172-13 Standard Practice for Proximate Analysis of Coal and Coke. Ultimate analysis of coal determines coal component elements that are Carbon, Hydrogen, Nitrogen, Sulfur, and Oxygen. This analysis is carried out according to ASTM D3176-15 Standard Practice for Ultimate Analysis of Coal and Coke. Bomb calorimeter is used in order to determine heating value of lignite and olive pomace.

3.4.2. Mechanical Characteristics

Coal briquettes should have some properties and the most important property is the mechanical durability of the briquettes. If briquettes are not strong enough, they may be disintegrated. Mechanical strength reveals the resistance of the briquettes against loading that occurs during various stages of production and utilization. In 1996, was published standard of coal briquettes for household heating- TS12055 by the Turkish Standards Institution in Turkey. According to this standard, coal briquettes should have certain physical and chemical properties. The most common tests carried out for controlling the durability of the briquettes are Shatter Test, Compressive Strength of the Briquettes, Tumbler Test, and Water Resistance.

According to this standard, the physical and chemical properties of coal briquettes are shown in Table 1.

Table 1. Mechanical Strengths of Coal Briquettes (TS12055)

Property	**Type I**	**Type II**
Shatter Test (%) , at least	90	80
Tumbler Test (%), at least	75	65
Compressive Strength (geometric shape of smooth base), kg/cm^2	130	100
Water Resistance, (%), at least	70	70

3.4.2.1. Test for Impact Resistance (Shatter Test)

This test shows the strength and the resistivity of briquettes against unloading from high places relatively. According to TS12055 Standard, briquettes are left to free falling from a height of a 120 cm for six times. After this, the screen analysis of the samples is being carried out with 10, 20, 31.5, 40, 50, 63, and 71 mm sieves for briquettes larger than 35 mm and with sieves of 5, 10, 16, 20, 25 and 31.5 mm for briquettes smaller than 35 mm. Each screen oversize mass is calculted as a percentage (C_i %). Samples between two sieves are calculated as the arithmetic mean of sieve openings ($L_{ave,i}$), mm. The minimum sieve opening is taken as 0, and the maximum sieve opening as an original briquette size as L, mm, (for λ +1). λ is the number of sieves. Average particle size (L_{ave}), mm, is calculated from formula below after the shatter test (TS12055, 1996).

$$L_{ave} = \frac{\sum_{i=0}^{\lambda+1} C_i x\, L_{ave,i}}{100}$$

After finding average particle size, L_{ave}, shatter index is found according to formula below as a percentage.

$$\text{Shatter Index (\%)} = \frac{L_{ave}}{L}\, x100$$

It is compared whether this value is appropriate or not.

3.4.2.2. Test for Abrasion Resistance (Tumbler Test)

The pulverization of the coal briquettes is measured with the tumbler. The objective of tumbler test is to determine the relative friability of the briquettes and their liability to disintegrate during all stages of production, transportation, and consumption (Altun, 2002). Procedure of this test begins with putting the briquettes inside the tumbler. The tumbler is rotated with a speed of 25 rev/min for 4 minutes. At the end of the test, screen analysis and calculations are done as same in shatter test (TS12055, 1996).

3.4.2.3. Test for Compressive Strength

Compressive strength is the resistance of material to break under compression. In other words, it is the measure of the volumetric breakage of the briquette. With the help of this test, the resistivity of the briquettes during compression and loading is measured.

This test is carried out by breaking the briquettes by compressing between two plates. The compressive strength against loading is determined for briquettes with flat bottoms. 10 briquettes are used for this test and arithmetic mean of these compressive strength values is found. Compressive strength value is compared whether this value is appropriate according to the values summarized in Table 1 or not (TS12055, 1996).

3.4.2.4. Test for Water Resistance

Coal briquettes need to be water proof for end use. Manufacturers encounter a problem of preserving the briquettes against undesirable weather conditions during transportation in open air or stockpiling conditions. However, there is no standard or test for this situation. For testing of the coal briquettes against water influence, a variety of methods are being used. Here, 20 briquettes are taken and 10 briquettes are left inside water for 1 hour. After drying the briquettes, they are broken in hydraulic press with two parallel plates and values are taken and the resistivity water resistance is calculated using the formula below (TS12055, 1996).

$$\text{Water Resistance } \% = \frac{T_s}{T_o} x100$$

In the formula, T_o is the average compressive strength value of 10 original briquettes and T_s is the average compressive strength value of 10 briquettes after being left in water.

3.5. Combustion Characterization of Fossil Fuels

The purposes of briquetting are mainly that coal briquettes should be strong and have good combustion property. The combustion of coal is a very complex reaction involving many parameters. The temperature at which the combustion of coal begins, maximum peak temperature (the temperature at which the maximum weight loss occurs), activation energy (the degree of easiness of the briquette to combust) of the reaction, calorific value, and residue at the end of combustion are some of the important variables that may change depending on the type and characteristics of the briquettes. Those factors vary according to the parameters involved during briquette production. Some of the important parameters that may affect the combustion characteristics of the briquettes are the origin of the coal, the size, applied load, binder used, etc. (Hiçyılmaz et all., 2000). Many researchers have studied number of studies about combustion characterization of coal briquettes containing a variety of fuels such as coal, asphaltite, oil shale, etc. Many techniques have been used in the literature to study the combustion of fuel. The combustion characteristics of the briquettes can be determined by using Thermogravimetry/Differential Thermogravimetry (TG/DTG) and Differential Scanning Calorimetry (DSC). The emission profiles of the blends were determined (particularly in terms of emission) by using Effluent Gas Analysis (EGA). For the combustion kinetics, Arrhenius Kinetic model was applied successfully.

Smith et al. (1981) investigated that combustion kinetics of coal with DTG for the temperature range of 25-900°C. Arrhenius kinetic model was applied using the results of the DTG analysis. The purpose of this is to determine the tendency of coal samples to combust. It was concluded that results of DTG analysis gave efficient results for the combustion of coals (Smith et al., 1981).

Kök et al., (1997) studied the combustion characterization of different oil shales from different regions from Turkey using thermogravimetric methods. The usage of various different kinetic methods were determined with different methods.

Combustion characteristics of Soma lignite were investigated using thermogravimetric analysis. TG/DTG curves of R.O.M and clean lignite were obtained for different particle sizes to study the effect of cleaning. Kinetic analysis were also carried out using Arrhenius Kinetic model. It was conculded that coal cleaning has an effective impact on combustion behaviour of lignite, combustion kinetics and thermal characteristics (Özbaş et al., 2000).

Yüzbaşı et al., (2011) studied the combustion behavior of indigenous lignite, olive residue and their blends containing 50% by weight in air and oxy-fuel conditions. In the study, TGA combined with Fourier Transform Infrared (FTIR) were used to investigate the behavior. DTG profiles of olive residue, lignite, and their blends were compared. Result of DTG curves show that initial weight loss due to moisture content occurred between 25°C and 200°C for all fuel samples and combustion environments. There are two stages for olive residue thermal and oxidative degradation in all combustion environments. The main weight loss occurred in 180-360°C as the first region. The second weight loss occurred in 360-600°C. In experimental combustion profiles of olive residue-lignite blends, some deviations were observed such as higher burning temperature and different maximum weight losses (Yüzbaşı et al., 2011).

3.6. Biomass

Energy need has been increasing day by day with population increase and developing technologies. This situation leads to the need of finding new resources around the world. One of these resources is biomass that can be used as energy and raw material for chemicals. For the last decades, biomass energy has been considered as an alternative to available energy sources. Biomass energy has found great opportunities for being environment friendly and an sustainable energy source, providing safe environmental management and targeting development throughout the world. For this reason, utilization of biomass energy has gained importance as an energy source in Turkey (Karayılmazlar et al., 2011). Forestry by products, bio solids, municipal solid wastes, industrial wastes, and agricultural remnants account for biomass materials. Biomass resources attract attention regarding their renewable nature and availability. Consequently, technologies have been applied to utilize the energy content in biomass through the power generation (Haykiri-Acma et al., 2013)

Biomass is the organic matter mass of plants and animals. Biomass energy is the energy obtained by the biomass sources. The source of this energy is solar energy. As a result of the conversion of carbon dioxide to organic compounds by photosynthesis, solar energy is stored as fixed carbon in the biomass. This is shown in the following equation below (Ulu, 2011).

$$nCO_2 + nH_2O + sunlight + chlorophyll \longrightarrow (CH_2O)_n + nO_2$$

$$\text{Solar energy} \longrightarrow \text{Chemical energy in plant}$$

There are positive aspects of using biomass as an energy sources;

- They are renewable energy sources.
- They are suitable for efficient energy conservation at all scales.
- They can grow in most of the places and can be stored.
- They can contribute to the social-economic development.
- They do not cause environmental pollution.
- They have very low ash content.
- They do not create greenhouse effect so they can balance amount of CO_2 in the atmosphere.

The mechanical strength of the briquettes produced from Kütahya - Seyitömer lignite can be improved by adding some biomass samples. Results show that water resistance of the briquettes can be improved by adding olive refuse. Of the biomass samples, olive refuse and paper mill waste can be used in the production of durable fuel briquettes (Yaman et al., 2000).

According to Biomass Energy Potential Atlas (BEPA, 2018) of the Ministry of Energy and Natural Resources, it is shown that biomass potential in Turkey is on the basis of Ton Equivalence Petroleum (TEP)/year as summarized in Table 2 (BEPA, 2018).

Table 2. Biomass Energy Potential in Turkey

Biomass Source	Energy Potential (TEP/year)
Plant Waste	39,877,285
Municipal Organic Solid Waste	2,315,414
Animal Waste	1,176,198
Wood Waste	859,899
TOTAL	**44,228,795**

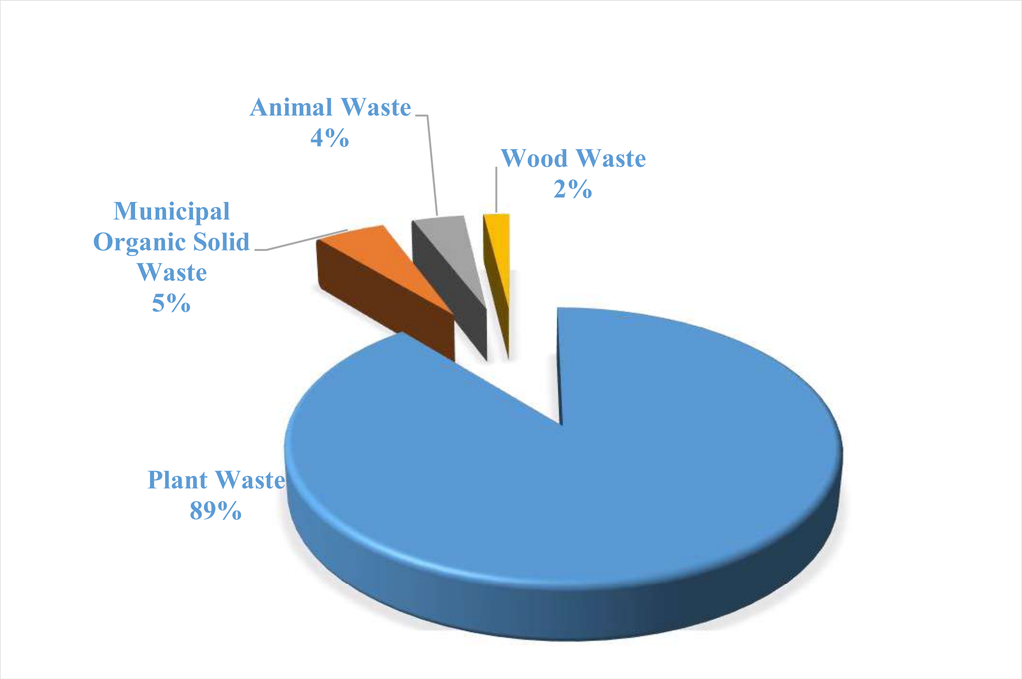


Figure 1. Biomass Potential Values (%)(BEPA, 2018)

In Figure 1, the highest amount of biomass potential source is plant waste as 89%. As a result, sources of biomass used in energy production are mainly plant sources.

Plant sources are agricultural wastes, forest products, tree species that grow 5-10 years, some algae and waterweed. Also, nut and nut shells, olive pomace, sunflower seed shells and sweet corn wastes can be used as energy sources. In Turkey, the annual amount of agricultural product waste is about 60 million tons and about 30-40 million tons are used for energy production (Dahilioğlu, 2008). Oil seed plants and olive wastes are also important biomass raw materials (Topal et al., 2008).

One of the most important biomass potentials is olive pomace which is a specific type of biomass. It is the remaining part of olives in factories and is accumulated in large quantities as waste as a result of olive farming activities (Yüzbaşı et al., 2011). Turkey is one of the leading countries in the world along with Spain, Italy and Greece in olive production. Olive agriculture and olive oil production concentrated in Aegean Region, Western Mediterranean and Southern Marmara Region. Balıkesir, Muğla, Gaziantep, and İzmir have the leading olive pomace factories (Tunalıoğlu, 2004). Olive pomace is actually rich in carbon, hydrogen, and nitrogen and besides these, it has very low content of sulfur, high calories of biomass source and it is a clean alternative energy source. According to Tunalıoğlu (2004), an average of 6-8 kg of residue oil from 100 kg of olive pomace and the rest is a potential of biomass.

According to Ministry of Environment and Urbanization & TÜBİTAK (Ministry of Environment and Urbanisation & TÜBİTAK, 2015), as a result of olive oil production in Turkey, there are about 643,000 ton/year of olive pomace.

Animal wastes are substantial in Turkey. The use of animal wastes as an energy source which is obtained by mixing and drying with straw is common in the villages. The total amount of dry waste obtained from sheep, goats, and bovines is 46 million tons. 10 % of this amount is used as fertilizer, 30 % of it is used for pasture areas, and 60 % of it is used for heating and cooking (Dahilioğlu, 2008).

CHAPTER 4

RESEARCH METHODOLOGY

In this study, selected lignite for briquetting on the basis of high sulfur and ash contents and low-to-medium calorific values and from Çanakkale and Tunçbilek lignite basins whereas Yatağan, Muğla olive pomace will be used as biomass source. In this briquetting process, molasses will be used and also molasses + lime, an inorganic binder, combination in laboratory works. The methodology involves;

a) **Determining the lignite specimen and thermal characterizations of lignite and olive pomace:** Fuel characteristics of lignite and olive pomace will be separately identified by proximate and ultimate analysis and by determining calorific values. The combustion (thermal) behavior of the blends will be investigated by Thermogravimetric/Differential Thermogravimetric (TG/DTG) and Differential Scanning Calorimetry (DSC). The emission profiles of the blends will be determined (especially SO_2 emission) by Effluent Gas Analysis (EGA).

b) **Thermal characterization of olive pomace-lignite blends:** Olive pomace and lignite will be blended with different proportions and thermal characterization of these blends.

c) **Determining the briquetting pressure, particle size and moisture of lignite specimens:** In this part, the strength of briquettes will be determined with parameters which are the particle size of -3 mm, -6 mm, -9 mm lignite, lignite specimens with 3%, 6%, 9%, 12%, and 15% of moisture content, and briquetting pressure at 1 ton, 2 tons, 3 tons, 4 tons, and 5 tons. Also, molasses will be added at 10%. Briquettes with homogeneous structure and length/diameter (L/D) ratio of briquettes is close to 1 as higher strength values are achieved compared to other shapes. (Asmatülıp , 1996). Thus, cylindrical briquettes with 5 cm length and 5 cm diameter will be used.

d) **Determining briquetting conditions for the olive pomace-lignite blends without binder:** In this stage, variables for olive pomace will be additive ratio (10-60%), moisture content (5-25%) and particle size (3-15 mm). As in the previous stage, the parameters will be changed one by one. While the ideal level of a parameter is determined, other parameters will be held at a fixed and a middle level. According to TS12055 (1996), the strength of the hybrid briquettes will be assessed by the strength tests; shatter test (drop), compressive strength of the briquettes for breakage, tumbler test for abrasion, and resistivity against water test.

e) **Briquetting olive pomace-lignite blends with binder:** Olive pomace-lignite blends will be briquetted with binder and they will be compared by their strength properties between briquetting using with and without binders. The most common used binders in the industrial are molasses and lime. Molasses (5-15%) and lime (0-6%) will be added varying amount. As in the previous stages of (c) and (d), parameters will be changed one by one. When the ideal level of molasses is achieved, ideal level of lime will be determined. In case there is a problem when using binders in briquetting process, the alternative binders with high binder properties will be classified and hybrid fuel briquettes will be obtained with these alternative binders.

During the preparation of blends, laboratory type crushers, representative sample separators, sieves, stirrer and laboratory type oven will be used at every stage. The prepared blends will be obtained by using a briquetting press and briquetting mold made out of steel.

CHAPTER 5

MATERIALS AND METHODS

5.1. Lignite Samples

In the first phase of the study, lignite fields used for the production of hybrid fuel were considered in terms of distance to the major olive production areas in the Aegean Region (Muğla, Aydın, İzmir, Balıkesir, Çanakkale) for olive pomace, waste material; having difficulties such as marketing and heating due to high ash, high sulfur content, and undesired combustion properties. Also, the lignite fields that can be operated in medium and long term were considered in terms of the amount of available reserves. Lignite areas in the Aegean Regions which are Yatağan, Soma, Tunçbilek and Çanakkale-Çan lignite were examined in terms of criteria that are ash content, sulfur content, reserve status, thermal value, and the condition of saleability. At the end of the study, sulfur and ash content, thermal value and strength properties of briquette are intended as a saleable product. The way to obtain a usable product as a result of the study is to take into account the applicable standards/criteria especially in terms of low sulfur and ash content and its thermal value and strength properties of briquettes. In other words, in order to determine the lignite samples to be used in the project in terms of saleability/usability, it is obligatory to observe the lower limit of thermal value and strength properties of briquettes. Hybrid fuel briquettes that must have thermal value and strength properties of briquette are considered as the TS12055 Standard. The thermal value and strength characteristics of briquette for selection of the lignite samples to be used in this study are shown in Table 3. Hybrid fuel, obtaining low ash and low sulfur content in the study, is targeted to be applicable for strength characteristics and lower calorific value, which is summarized in Table 3 for Type I briquette = 5000 kCal/kg and for Type II briquette = 4000 kCal/kg) described in

TS12055 standard. In addition, the main characteristics of the olive pomace used in this study have also been determined and lower calorific value of olive pomace is around 4500 kCal/kg as shown in Table 6. Even when considering the lower calorific value requirement of 4000 kCal/kg (Table 3) and lower calorific value of olive pomace approximately 4500 kcal/kg for Type II briquettes (Table 6), the hybrid-fuel briquette to be obtained by using local low thermal value of briquettes will not be possible to provide the criteria for lower calorific value required for the briquettes- despite the improvement in the amount of 50 % olive pomace.

Therefore, in order to transform the study outputs into a product, lignite fields which are likely to be evaluated in the form of hybrid fuel were taken into account in terms of their thermal value.

Table 3. The properties of coal briquettes according to TS12055 standard

Property	**Type I**	**Type II**
Lower Calorific Value (kCal/kg), at least	5000	4000
Impact Resistance (%), at least	90	80
Abrasion Resistance (%), at least	75	65
Compressive Strength (smooth base briquette, kg/cm^2), at least	130	100
Water Resistance (%), at least	70*	70*
Sulfur Emission (%), at most	0.8	1.0

*not required for briquettes sold in waterproof packing

In this assessment, Yatağan lignites are not likely to meet the thermal value criteria for hybrid fuel briquettes and low amount of reserves. Soma lignite receded into background in this study due to the more favorable fuel properties and less problematic for heating purposes compared to other basins. Tunçbilek and Çan lignite were identified as lignite samples used in this study such criteria that adverse fuel characteristics with high ash or/and sulfur contents, not suitable for heating purposes, and their high reserve potential. After determination of the lignite samples, run-of mine lignite taken from two sites were characterized. The results of the proximate and ultimate analysis of Tunçbilek and Çan lignite samples as received basis and dry basis are shown in Table 4 and 5.

Table 4. Proximate analysis results of Kütahya-Tunçbilek and Çanakkale-Çan lignite samples

	Tunçbilek Lignite		**Çan Lignite**	
	Received Basis	Dry basis	Received Basis	Dry Basis
Moisture, %	6.20	-	10.19	-
Volatile matter, %	28.99	30.91	39.45	43.92
Ash, %	23.12	24.64	15.21	16.94
Fixed Carbon, %	41.69	44.45	35.15	39.14
Lower Calorific Value, kCal/kg	5590.12	5959.62	5350.56	5957.64

Table 5.Ultimate analysis results of Kütahya-Tunçbilek and Çanakkale-Çan lignite samples

	Tunçbilek Lignite		**Çan Lignite**	
	Received Basis	Dry Basis	Received Basis	Dry Basis
Carbon (C), %	59.87	63.83	56.13	62.49
Hydrogen (H), %	6.32	6.74	5.72	6.37
Nitrogen (N), %	3.54	3.77	2.52	2.81
Sulfur (S), %	2.48	2.64	5.96	6.64

When the results in Table 4 and 5 are evaluated, it is unlikely that Tunçbilek Lignite can be marketed as high sulfur and nearly high ash content and also Çan Lignite are not be able to be marketed as run-of-mine for heating purposes due to its high sulfur content. In addition, as thermal values, the calorific value of the hybrid fuel (even in the 50 % olive pomace addition) is likely to reach the limit values for both Type I and Type II briquettes in standard TS12055. Therefore, both lignite samples have the potential to be suitable for the addition of olive pomace for the fuel properties and usable hybrid fuel briquettes. However, the briquetting properties of coal are also important for the production of hybrid fuel briquettes. At this point, it is aimed to meet the limit strength values in TS12055 standard. The tendency of both coal belonging to different regions was discussed at the beginning of the study to avoid briquetting problem in the later stages of the project.

In this context, preliminary briquetting studies were carried out for both lignite samples. Lignite particles with a size of – 6 mm were pressed under 3 tons load with the addition of 10% molasses and 5% water to obtain a large number of briquettes. As a result of this evaluation, it was observed that Çan lignite could not be removed from the briquette mold in one piece after the load application and the parts removed from the steel mold could not maintain their integrity in any way. Çan lignite was studied without addition of water, higher load application (4 and 5 tons), using a higher amount of binders (15% molasses), and briquetting with finer size particles (-3 mm) but the result did not change. It is understood that Çan briquettes that can be subjected to mechanical durability tests could not be obtained. On the other hand, preliminary briquetting works of Tunçbilek lignite shown good results and briquettes were obtained in one piece from briquette molds without any problem. Therefore, it was decided to use Kütahya- Tunçbilek lignite for the production of hybrid fuel briquettes in the later stages of the study.

5.2. Characterization of Lignite and Olive Pomace Samples

In the decision of the lignite sample used in the study, a sample of olive pomace is provided from Muğla region which is an intense olive production area. The basic fuel characteristics of the lignite sample are given above. The results of the proximate and ultimate analysis of olive pomace used in the study are shown in Table 6. Furthermore, both lignite and olive pomace are subjected to X-Ray Diffraction (XRD) analysis. In Figure 2 and 3, X-ray diffractions of lignite and olive pomace are given.

Table 6. Results of proximate and ultimate analysis of olive pomace sample

Proximate Analysis	Received Basis	Dry Basis	Ultimate Analysis	Received Basis	Dry Basis
Moisture, %	11.56	-	**Carbon, %**	46.12	52.15
Volatile matter, %	58.58	66.24	**Hydrogen, %**	6.99	7.90
Ash, %	2.68	3.03	**Nitrogen, %**	0.00	0.00
Fixed Carbon, %	27.18	30.73	**Sulfur, %**	0.00	0.00
Lower Calorific Value, kCal/kg	4533.01	5125.5			

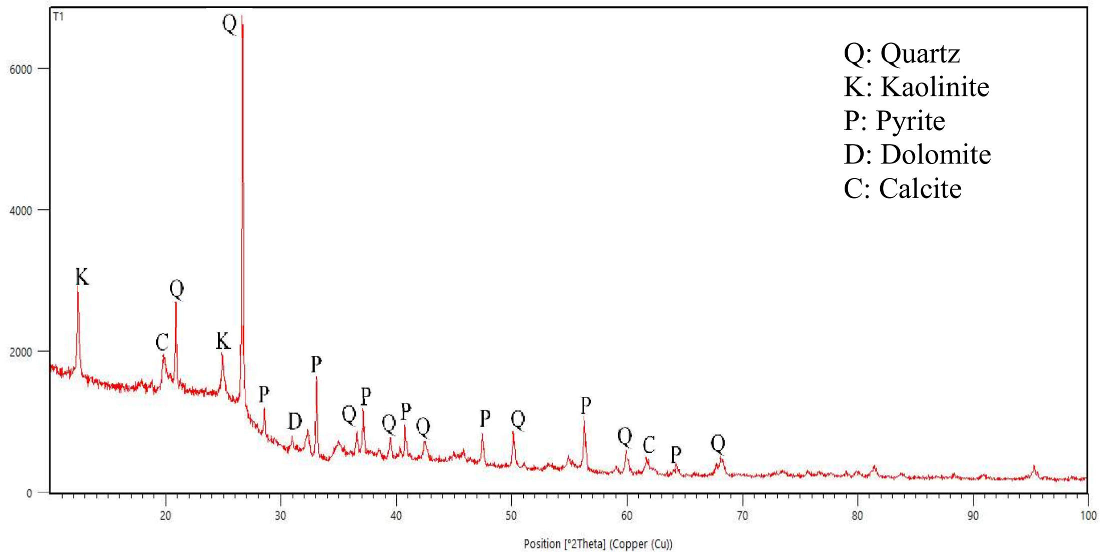


Figure 2. X-Ray diffraction of run-of-mine Tunçbilek lignite sample

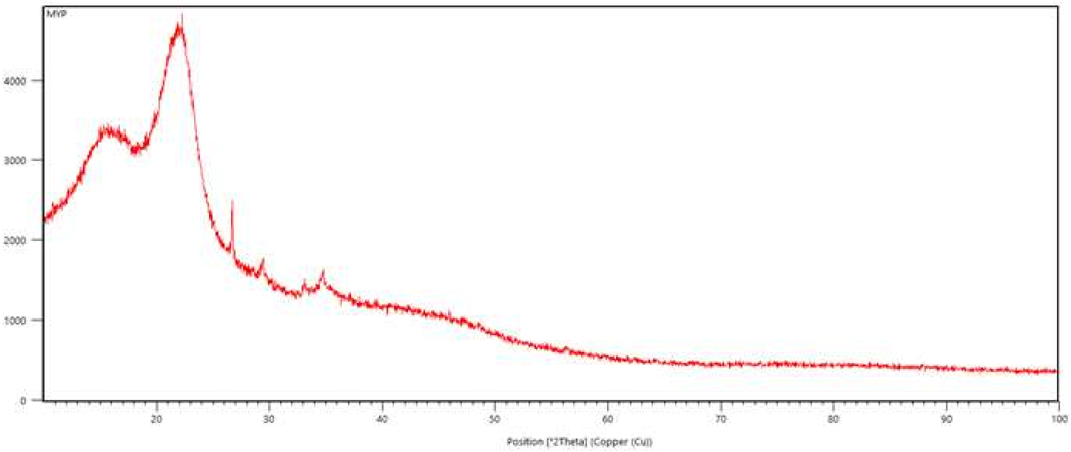


Figure 3. X-ray diffraction of original olive pomace

As shown in Figure 2, the inorganic content of the lignite sample is mostly composed of quartz and pyrite, and in the lignite sample, pyrite is an important source of Sulfur. Besides these two minerals, the presence of kaolinite and carbonate minerals (calcite and dolomite) were also observed. The X-ray diffraction of olive pomace sample is characteristic. Especially, the region between 10° (2Θ) and 25° (2Θ) is quite different from lignite sample and the wide region that are the peaks about 10° (2Θ) and 22.5° (2Θ), and 26° (2Θ) and 34.5° (2Θ) are remarkable. The region giving a peak between 5 -18° (2Θ) and 10° (2Θ) corresponds to the amorphous cellulosic content in the structure of the olive pomace. Also, peaks in the wide region between 18-28° (2Θ) and 22.5° (2Θ), and peaks around 28° (2Θ) and 34.5° (2Θ) corresponds to the crystalline cellulosic content of the olive pomace. In other words, the cellulosic content of the olive pomace is more dominant. The X-ray diffraction of the olive pomace, which does not contain any indicative formation except the stated region and peaks, is quite a simple structure compared to the X-ray diffraction of the lignite sample.

5.3. Thermogravimetric Analysis and Determination of Combustion Properties of Fuels

The thermal behavior of lignite and olive pomace samples and lignite-olive pomace blends in the oxidizing environment, in other words, their combustion behavior and properties were determined by Thermogravimetry/ Differential Thermogravimetry (TG/DTG), Differential Scanning Calorimeter (DSC) and Effluent Gas Analysis (EGA) methods. In addition to separately identifying the combustion properties of lignite and olive pomace samples, lignite-olive pomace blends containing olive pomace ratio of 10%, 20%, 30%, 40% and 50% by weight were also subjected to these analyses to determine the above mentioned combustion behaviors. TG/DTG, DSC, and EGA between 30-900°C were carried out in a controlled manner with a constant temperature increase of 10°C/min and a constant oxygen flow of 20 ml/min. EGA determined the emission profiles of lignite and olive pomace samples during thermal behaviors in oxidizing environment and especially the effect of olive pomace on SO_2 emission was clearly revealed.

For the TG/DTG and DSC analyses, Perkin Elmer STA6000 Thermal Analysis System was used. EGA consists of Fourier Transform Infrared (FTIR) (Perkin Elmer Spectrum Two) with a specific connection system that transmits the gases emitted from the STA6000 Thermal Analysis System. This simultaneous system analyzes the emissions generated by the combustion of the samples between 30-900 °C and gives the emission profiles of the samples at the desired time/temperature. Thermal Analysis and Effluent Gas Analysis systems are shown in Figure 4.

Figure 4. Thermal Analysis System used for TG/DTG and DSC and Integrated gas transfer/FTIR used for EGA

5.4. Determination of Tendency to Combustion of Fuels and Kinetic Analyses

By using data obtained by Thermogravimetric Analysis, besides the thermal behaviors of fuels, their tendency to burn can be determined. The kinetic analysis of combustion reactions was performed by using various models on the obtained DTG data. Thus, the Activation Energy, obtained this way, reveals the tendency of the fuel to combust (or thermal reaction). By the kinetic analysis method, the change in the tendency of a particular fuel to burn due to various and/or changing conditions can be evaluated and the tendency of different fuels to burn can be considered comparatively.

In this study, DTG data obtained to determine and compare the tendency to burn for lignite sample, olive pomace and also hybrid fuel obtained from blend of these two organic materials were subjected to kinetic analysis. Another aim of kinetic analysis is to reveal the possible changes in the tendency of burning of hybrid fuel due to the varying proportions of olive pomace in olive pomace-lignite blends. Therefore, blends containing varying proportions of olive pomace with 10%, 20%, 30%, 40%, and 50% were subjected to kinetic analysis separately and in detail.

For kinetic analyses, Arrhenius Kinetic Model that is very compatible with DTG data and providing reliable result was used. The basic model is based on the following equation;

$$\left(\frac{dw}{dt}\right) = A \exp\left(\frac{-E_a}{RT}\right) w^n \qquad (1)$$

where

dw/dt	: the change of the weight of material to time-dependent
A	: the Arrhenius constant
E_a	: the activation energy (kJ/mol)
T	: temperature (K)
R	: the gas constant (=8.314 J/molK)
n	: the reaction order
w	: the material weight

In the analysis of TG/DTG data by Arrhenius model, it is assumed that the weight loss of material is only dependent on the rate constant and the weight of remaining of material, and the reaction (especially for fuels) is a first order reaction. Based on these assumptions, the equation (1) is as follows:

$$\frac{1}{w}\left(\frac{dw}{dt}\right) = A \exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

When the logarithm of both sides of equation (2) is taken, the following equation is obtained;

$$\log\left[\frac{1}{w}\left(\frac{dw}{dt}\right)\right] = logA - \frac{E_a}{2.303RT} \quad (3)$$

When $\log[\frac{1}{w}(\frac{dw}{dt})]$ and $\frac{1}{T}$ are plotted, the slope of the line is equal to $-\frac{E}{2.303R}$. The value of the curve in the y axis corresponds to the Arrhenius constant.

As stated above, Arrhenius model is a kinetic analysis method which is very compatible with TG/DTG data, especially in determining tendency of thermal reactions and burning of organic materials and fuels. However, the thermal behavior of fuels is a chemical phenomenon that does not consist of a single reaction in a highly complex structure. This thermal behavior consists of successive chain reactions. Moreover, depending on the type of fuel, the number of independent reaction regions may change. Thus, it is not an accurate approach to take the kinetic analysis profile obtained by DTG data as a whole, and obtain an activation energy for the whole profile, especially for fuels with more than one reaction region is observed. Applying the Arrhenius Kinetic Model for this type of material/fuels, "Weighed Mean Activation Energy" approach has been developed to determine the regional activation energies. The activation energies of the different reaction regions can be determined separately using the following equation, then these values are summed up and a cumulative activation energy value for the fuel is found.

$$E_{wm} = F_1E_1 + F_2E_2 + F_3E_3 + \cdots + F_nE_n \quad (4)$$

In the equation above;

E_{wm} : "Weighted Average Activation Energy" for fuel,

$F_1, F_2, F_3, \ldots, F_n$: the percentage weight loss occurring in the reaction regions where combustion occurs,

$E_1, E_2, E_3, \ldots, E_n$: the activation energies of reactions regions where combustion occurs.

In this approach, the contribution of activation energy of any region to the cumulative activation energy depends on the weight loss in the reaction region, in other words, the intensity and magnitude of reaction. This allows the relatively more severe weight loss reactions to be accurately represented in the combustion of fuel. This method, thus, provides an important correction/improvement to the classic Arrhenius approach for fuels/materials showing more than one combustion/thermal decomposition reactions.

5.5. Briquetting Studies, Mechanical Strength Tests and Determination of Ideal Briquetting Conditions

In the first stage, in order to obtain a hybrid biomass-fossil fuel briquette, which is the main target of the project and which will be composed of lignite-olive pomace blends, only briquetting of the lignite sample was carried out. The first aim is to obtain briquettes that can maintain integrity with the lignite sample used, and the second one is to determine the strength characteristics of these briquettes and to form the ideal briquetting conditions for lignite-olive pomace blends. In addition, the strength properties of briquettes obtained using only lignite sample will provide a basis for comparing and evaluating the strength characteristics of hybrid fuel briquettes.

At this stage, the briquetting properties of Tunçbilek lignite were evaluated for lignite particle size (-3, -6, -9 mm), water addition (3, 6, 9, 12, 15%) and briquetting load (1, 2, 3, 4, 5 ton). The briquettes obtained with these variables were tested according to the methods specified in TS12055 in terms of compressive strength, abrasion resistance, impact resistance, and water resistance and the ideal briquetting conditions were determined. In the first stage of briquetting, molasses was used as binders. The lignite-molasses-water blends were mixed homogeneously in the laboratory type mixer, shown in Figure 5. Then, mixtures were subjected to briquetting under constant pressure using the steel mold, shown in Figure 6, to obtain cylindrical and flat-bottomed briquettes having a diameter and length of 5 cm. A laboratory type briquetting press used for briquetting is shown in Figure 7 and some of the briquettes obtained at certain stages and subjected to the test in Figure 8.

Figure 5. Laboratory type mixer for homogenization of lignite-binder-water blends

Figure 6. Steel mold using for briquetting mixtures

Figure 7. Laboratory pressure press for briquetting and strength tests

Figure 8. Some examples of lignite briquettes under various conditions

As mentioned above, the lignite briquettes obtained under various conditions were evaluated for their compressive strength, abrasion resistance, impact resistance and water resistance. These strength properties were carried out according to the procedure specified in TS12055. The procedures outlined below can be seen in detail in TS12055.

a) *Test for Impact Resistance (Shatter Test):* 10 briquettes were left free falling from height of 120 cm and this process has been repeated six times. After this, the screen analysis of the components of briquettes were passed through 10, 20, 31.5, and 40 mm sieves to determine the weight of the material under the screen and the weight of the material below 10 mm. The drop resistance values of the briquettes are calculated by using equations (5) and (6) using sieve sizes and amount of oversize material. As described in the standard, the smallest sieve opening in the calculations is 0 (for i =0) and the largest sieve opening is taken for the original briquette size (for λ + 1, 50 mm in this study).

$$l_{ave} = \frac{\sum_{i=0}^{\lambda+1} c_i l_{ave,i}}{100} \qquad (5)$$

$$SI\ (\%) = \frac{l_{ave}}{l} x100 \qquad (6)$$

Equations in above;

λ : the number of sieve

l_{ort} : the average particle size of sample after shatter test

c_i : the weight percentage of sample oversize of sieve i and passing through the i+1

l : the diameter of briquette (mm)

$l_{ort,i}$: the average aperture size of i and (i+1)

SI : Shatter Index (%)

Shatter index is expected to at least 90% for Type I briquettes and 80% for Type II briquettes in TS12055 standard. In this study, it was evaluated whether the briquettes obtained under different conditions provide these conditions.

b) *Test for Abrasion Resistance (Tumbler Test):* 10 briquettes were placed in the tumbler and the drum was rotated 100 revolutions at 25 rev/min. at the end of the test, briquette pieces in the drum were passed through 10, 20, 31.5, and 40 mm sieves to determine the weight of the material which was under 10 mm sieve. Sieve sizes and weight of oversize material were used to calculate the abrasion resistance of briquettes with the calculation the method of shatter test. Abrasion resistance is expected to be at least 75% for Type I briquettes and 60% for Type II briquettes in TS12055 standard. Then, it was evaluated whether the briquettes obtained under different parameters provide these conditions.

c) *Test for Compressive Strength:* 10 briquettes with physical integrity, no fracture or cracks were used. Each briquette was placed between two parallel plates and load was applied to each briquette from a vertical axis using a controlled hydraulic press. Load value of the briquette at the time of failure was determined and arithmetic mean of the values obtained for 10 different briquettes was calculated and then compressive strength was calculated. Compressive strengths for flat base shaped briquettes is expected to have at least 130 kg/cm^2 for Type I briquettes and at least 100 kg/cm^2 for Type II briquettes. Then, it was evaluated whether the briquettes obtained under different conditions provide these conditions.

d) *Test for Water Resistance:* 20 briquettes with physical integrity, no fracture or cracks were used. 10 of these briquettes without being placed in water were subjected to compressive strength test in controlled hydraulic press as described in the previous step. Load value of the briquette at the time of failure was determined and arithmetic mean of the values obtained for 10 different briquettes was calculated and then compressive strength of briquettes without being placed in water was calculated. Then, other 10 briquettes were left in water for 1 hour. After 1 hour these briquettes were removed from the water, they were subjected to compressive strength test in press. Load value of failure of each briquette placed in water was determined. The arithmetic mean of the values obtained for 10 different briquettes was calculated and compressive strengths of the briquettes left in water were calculated. Then, using these two values, water resistance of the briquettes was determined according to the following equation;

$$WR\ (\%) = \frac{T_S}{T_O} x100 \qquad (7)$$

Equations in above;

WR : Water resistance, %

T_S : the average load value of failure of briquettes left in water, kgf

T_O : the average load value of failure of original briquettes, kgf

In TS12055 standard, water resistance is expected to be at least 70% for both Type I and Type II briquettes selling unpacked. However, this property is not asked for briquettes that are in closed bags and/or in waterproof packaging. In the study, it was determined that the briquettes with molasses as binders could not perform well for the water resistance condition. In fact, this is valid for briquetting of almost all of Turkish lignite resources. In almost all industrial briquetting processes; molasses is used because of their low cost and abundance, effective binding nature and high strength properties to briquettes, organic structure and environmental advantage during and after combustion. However, molasses is a residual product that is produced as a result of sugar beet and does not give water resistance to the briquettes. The same situation was encountered in this study. Hybrid-fuel briquettes to be obtained are foreseen to be marketed as stated in the standard.

CHAPTER 6

RESULTS AND DISCUSSION

6.1. Investigation of Combustion Characteristics of Lignite and Olive Pomace

Thermogravimetry, Differential Thermogravimetry and Differential Scanning Calorimetry were used to determine the combustion characteristics of Tunçbilek run-of-mine lignite and olive pomace samples.

Thermogravimetry, Differential Thermogravimetry and Differential Scanning Calorimetry profiles of Tunçbilek run-of-mine lignite are given Figure 9, 10 and 11, respectively. As it can be seen in Figure 9 and 10, weight losses were observed at four different ranges as a result of burning of Tunçbilek lignite in the oxygen environment in a controlled manner. The first one of these is the region about between 50 °C and 110 °C where Tunçbilek lignite losses its moisture content. The second region is between 250 °C and 300 °C corresponding to the volatile loss and burning of volatile organic compounds. The third weight loss was observed in the region of approximately between 300 °C and 410 °C. As it can be seen from the DTG profile, it was observed that there is a reaction region with a significant weight loss as a result of the burning of the organic content of Tunçbilek lignite. Following this region, the weight loss continues between 410 °C and 590 °C and it can be said that this weight loss is due to an exothermic reaction predominantly related with burning of the organic content of lignite. The amount of material remaining in the result of TG analysis ending approximately at 900 °C is 20.21 %.

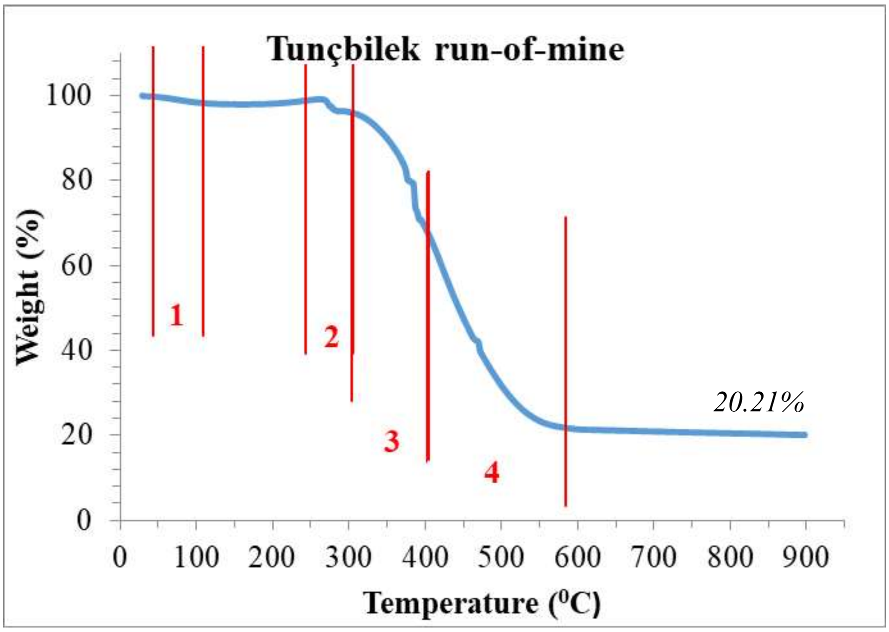


Figure 9. Thermogravimetry profile of Tunçbilek run-of-mine lignite sample

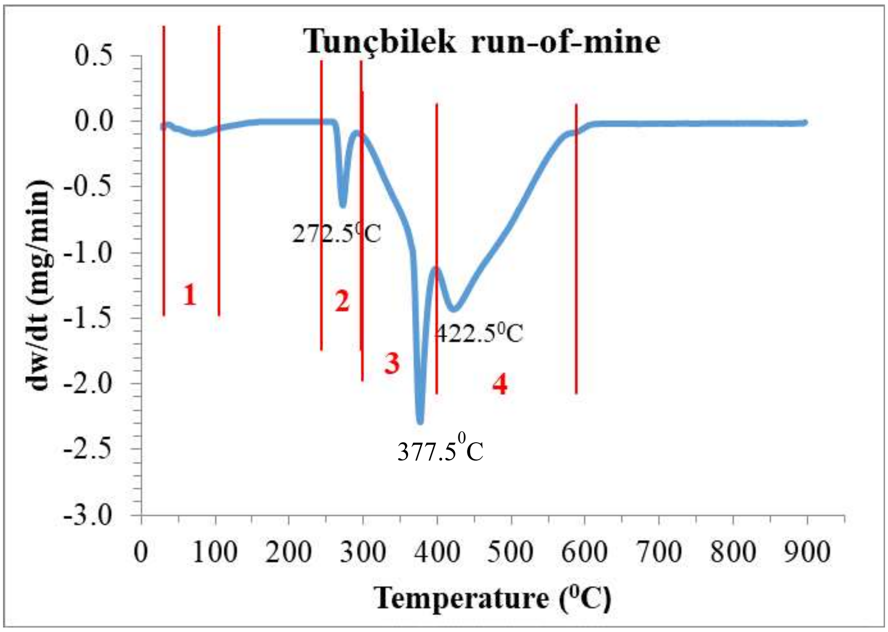


Figure 10. Differential Thermogravimetry profile of Tunçbilek run-of-mine lignite sample

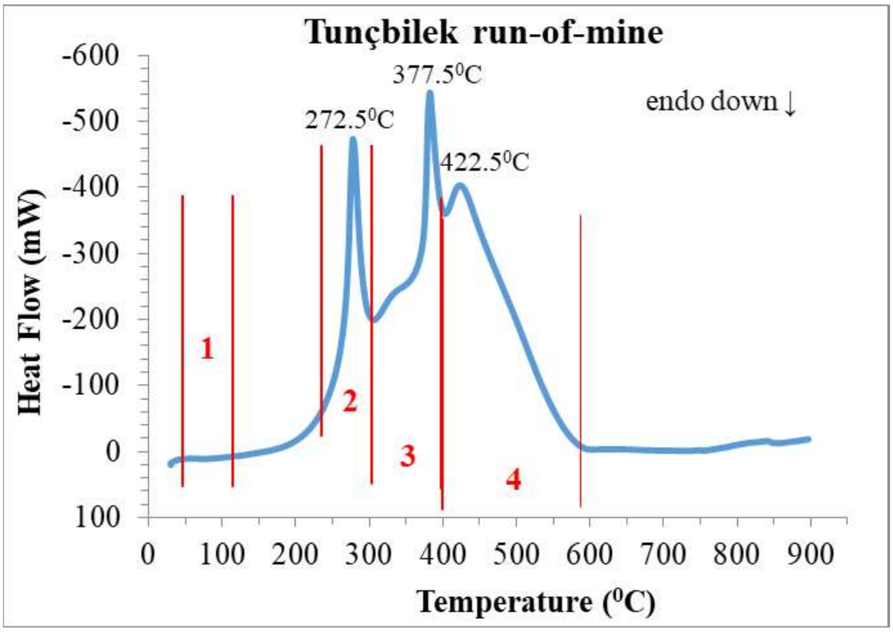


Figure 11. Differential Scanning Calorimeter profile for Tunçbilek run-of-mine lignite sample

As a result of the evaluation of the TG- DTG profiles, in DTG profiles, the temperature at which DTG profiles reach the most severe point of the reaction, especially from the temperature ranges in which the significant weight loss occurs, can be determined and these points are called “peak temperatures”. In this regard, the peak temperature of the 2^{nd} reaction region was determined as 272.5 °C, the peak temperature of the 3^{rd} reaction region was determined as 377.5 °C and the peak temperature of the 4^{th} reaction region was determined as 422.5 °C (Figure 10).

In the DSC profiles, the downward direction corresponds to the endothermic, in other words, heat absorbed by sample reaction regions, while the upward direction corresponds to the exothermic, in other words, heat released by sample reaction regions. Exothermic regions observed in the DSC profile, the peaks observed in these regions and the intensity of these peaks are important factors in determining the thermal efficiency of the fuel sample. It can be seen that the DSC profiles of Tunçbilek rom lignite appears to be in harmony with the TG/DTG profile. With this regard, exothermic peak was not observed for the weight loss region where moisture loss occurred. However, the exothermic reaction regions which correspond to the 2nd, 3rd, and 4th reaction regions in which the thermal oxidation of organic content of lignite occurs, varying width and peak intensity was significantly observed (Figure 11). In addition, the temperatures at which these exothermic peaks occur and the peak temperatures observed in the DTG profile coincide with each other. Also, these temperatures, at which exothermic peaks occur, confirm the points at which the combustion reaction reaches the highest intensity in the reaction regions. In other words, in thermal oxidation of Tunçbilek lignite, it can be seen that 2nd, 3rd and 4th regions are the intervals in which combustion occurs. The most effective combustion reaction takes place especially in the 3rd region. Correspondingly, at this region, time-dependent weight loss and heat discharge reached the highest point (Figure 10 and 11).

TG and DTG profiles of olive pomace are shown in Figure 12 and Figure 13, DSC profile is shown in Figure 14. As a result of burning of olive pomace sample in the oxygen environment, weight loss was observed at four different regions. The 1st region is between 50 °C and 110 °C where the olive pomace was lost its moisture content. The 2nd region corresponds to the combustion reaction between 210 °C and 340 °C. The 3rd weight loss is observed in the region approximately between 340 °C and 365 °C. Following this region, weight loss continued between 410 °C and 490 °C and this region is the last apparent reaction region in the TG/DTG profile of the olive pomace. The amount of material remaining in the result of TG analysis ending approximately at 900 °C is 0.91 %.

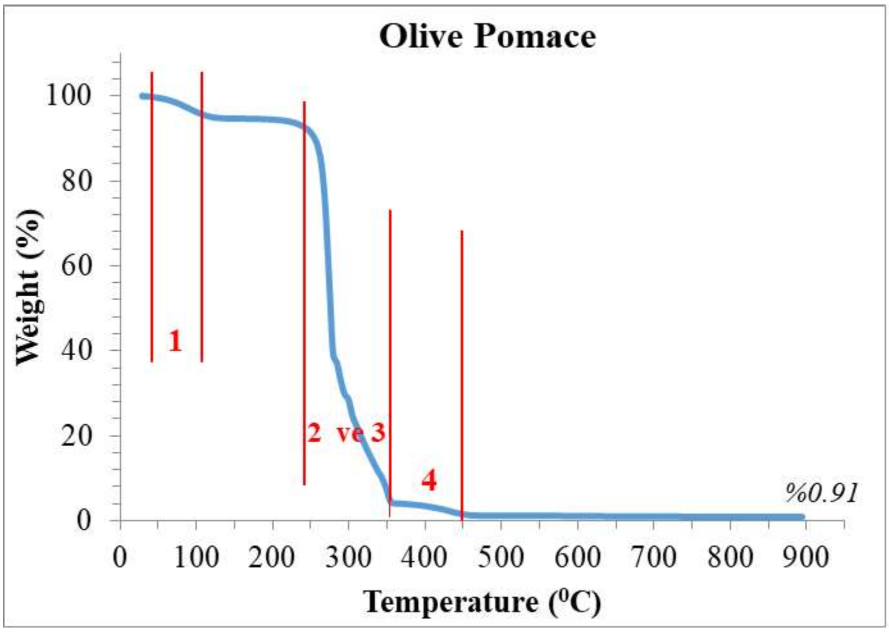


Figure 12. Thermogravimetry profile of olive pomace sample

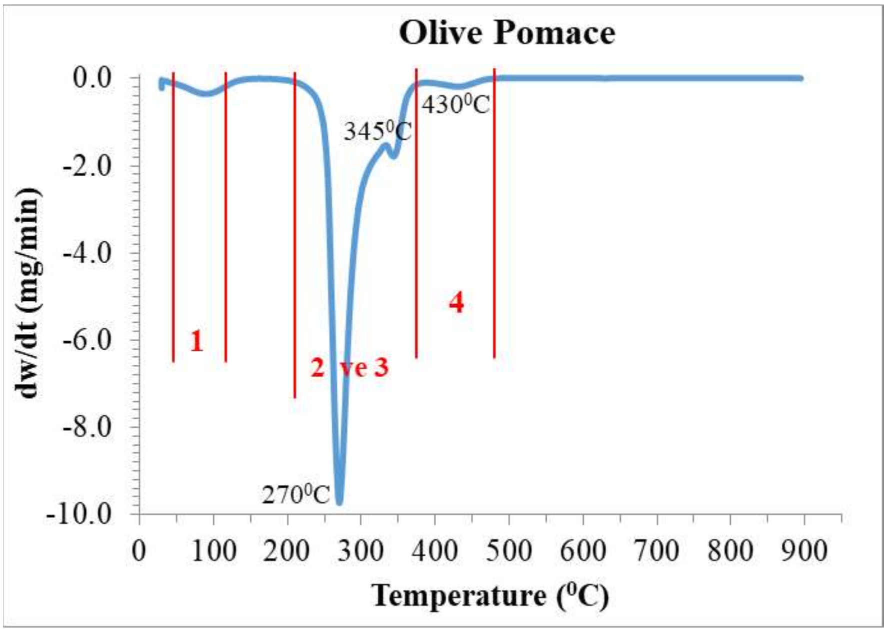


Figure 13. Differential Thermogravimetry profile of olive pomace sample

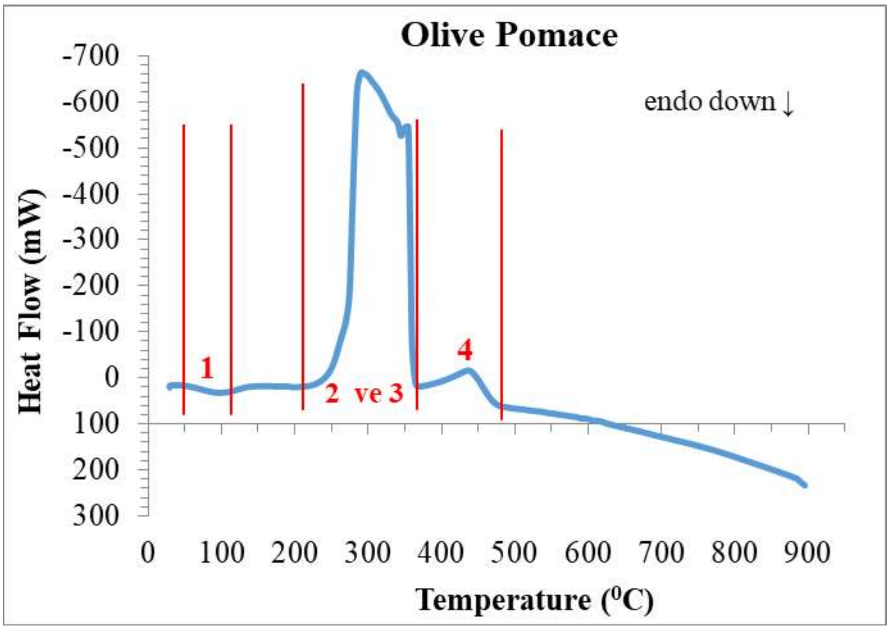


Figure 14. Differential Scanning Calorimetry profile of olive pomace sample

Considering the TG/DTG profiles of olive pomace (Figure 12 and 13), it was observed that the combustion behavior of the olive pomace was quite different from the lignite sample. Moisture loss region is similar but moisture loss is more (≅ %4). In addition, when the regions where the organic content of olive pomace burnt out are considered, the combustion in the 2nd region caused a much higher weight loss, a high peak was observed as a result of this high weight loss. As a result of the combustion reaction in the 3rd region, a lower weight loss occurred. Weight loss in 4th region occurred as a characteristic of exothermic reaction and when this reaction is compared to the 3rd region, it has a wider temperature range. When observing the peak temperatures at which weight losses reached the highest speed; it is seen that the peak in 2nd region is at 270 °C, the peak in 3rd region is at 345 °C and the peak at 4th region is at 430 °C (Figure 13). Furthermore, remaining material amount (0.91%) at the end of 900 °C was much lower than the value obtained as a result of the combustion of lignite (20.21%). This indicates that olive pomace has a very limited content in terms of inorganic and ash-forming material. When the peaks obtained in the DTG profile are evaluated, the intensity of peak of the 2nd region shows that the organic content of olive pomace is narrower temperature area and burns more intense (Figure 13). The DSC profile of olive pomace appears to be consistent with the TG/DTG profile (Figure 14). The 1st region where moisture loss occurs is endothermic type. The successive structure of 2nd and 3rd reaction regions in the TG/DTG profiles was also observed in the DSC profile. Accordingly, a large and severe exothermic reaction region was formed in the range of 210 - 380 °C. At the end of this exothermic reaction region, another exothermic reaction corresponding to the 4th weight loss region observed in the DTG profile was observed (Figure 14). The heat generation profile observed in this region is lower than the 2nd and 3rd regions and this situation confirms the TG/DTG profile. Exothermic reaction region and peaks observed in the DSC profile coincided with the reaction regions and weight losses in the DTG profile.

6.2. Investigation of Combustion Characteristics of Lignite and Olive Pomace Blends

Following the determination of thermal properties and behaviors of lignite and olive pomace samples separately, another stage of investigating the thermal behaviors of mixtures containing different proportions of olive pomace and lignite to be used in the formation of hybrid-fuel briquettes was initiated. In this regard, TG/DTG and DSC profiles of the lignite and olive pomace blends containing 10, 20, 30, 40, and 50 % by weight of olive pomace were obtained.

Figure 15 and 16 show the TG and DTG profiles of the blends containing 10% by weight of olive pomace and Figure 17 shows the DSC profile of the same sample. In the TG profile, after the region showing the moisture loss (at 100°C), three weight losses region was clearly seen (Figure 15). These regions, as seen from the DSC profile, are the regions where exothermic reactions take place, in other words combustion occurs in these regions (Figure 17). The peak temperature, at the moment at which the combustion reaction takes place at the highest speed, in the first combustion region is about 255°C, indicating where the fastest weight loss occurs.

The peak temperatures of second and third region are approximately 345°C and 395°C, respectively (Figure 16).

It should be noted that after olive pomace addition, the DTG region of the first combustion region becomes more indicative compared to the run-of-mine lignite sample and the peak of the same region also comes to exist more severely. The DSC of the same peak also indicates a higher exothermic reaction. Also, the temperature range containing the third combustion region enlarges. At the end of the analysis at 900°C, the amount of remaining material is 19.00 %.

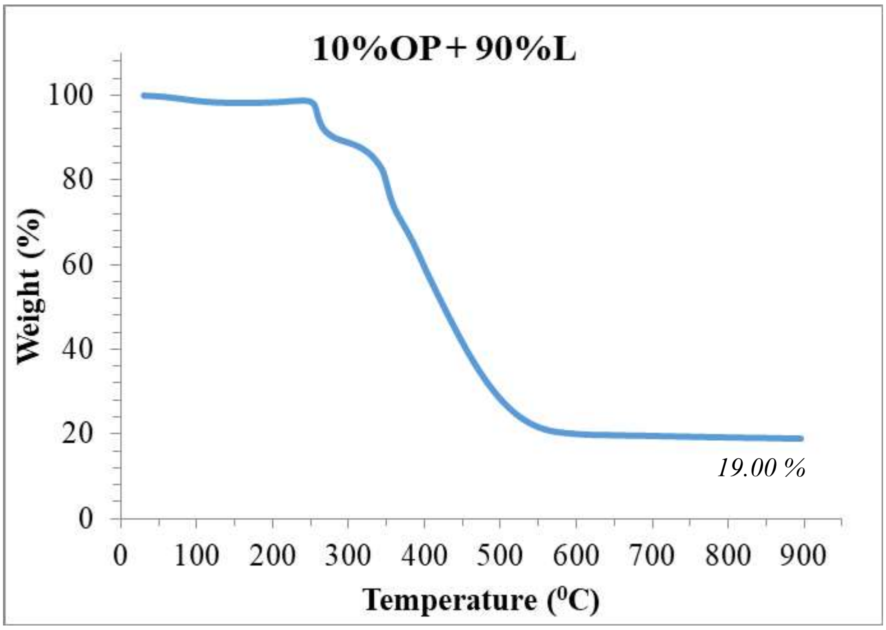


Figure 15. Thermogravimetry profile of the mixture containing 10% by weight of olive pomace

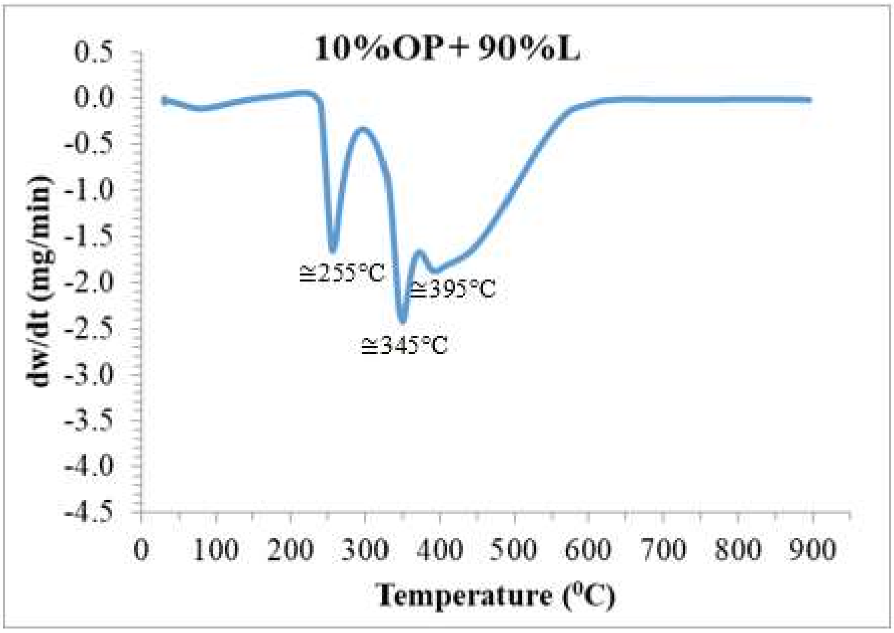


Figure 16. Differential Thermogravimetry profile of mixture containing 10% by weight of olive pomace

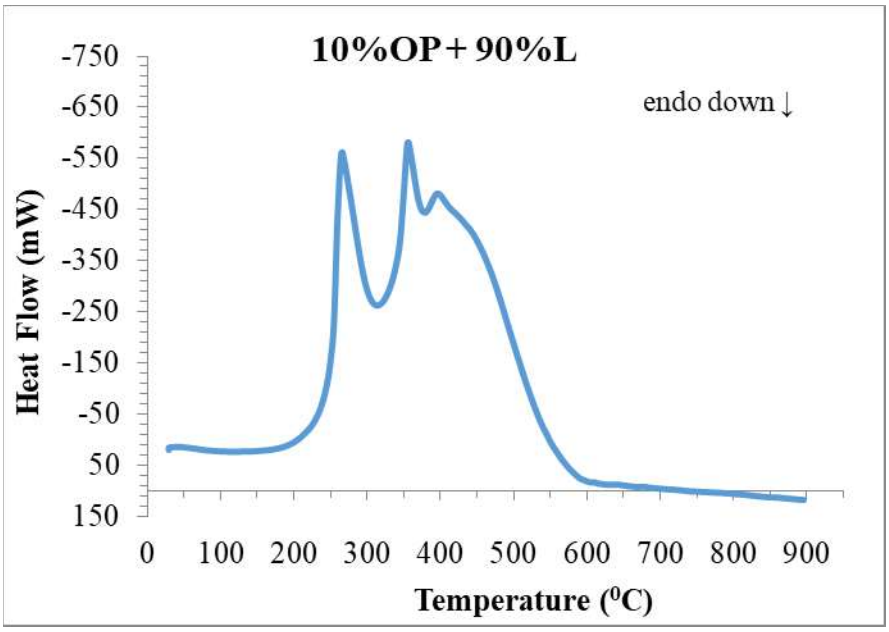


Figure 17. Differential Scanning Calorimeter profile of mixture containing 10% by weight of olive pomace

TG and DTG profiles of blends containing 20% by weight of olive pomace are shown in Figure 18 and 19, DSC profile of same sample is shown in Figure 20. In TG profile, three weight loss regions were observed apparently after loss in moisture content (Figure 19). These are exothermic combustion reaction regions as seen in the DSC profile (Figure 20). The peak temperature of the first combustion region is approximately 255°C, the peak temperature of the second region is approximately 345°C and the peak temperature of the third region is nearly 400 °C (Figure 19). When profiles belonging to this sample are compared with the profiles of the lignite and blends of 10% olive pomace, it is clearly seen that the intensity of the first combustion region is much higher. The intensity of the second combustion region is higher than that of the 10% olive pomace (Figure 19). In the DSC profile, the first and second exothermic regions, whose intensity and width are increasing, indicate an increase in combustion along with increase in olive pomace ratio (Figure 20). The amount of remaining materials of blends containing 20% by weight of olive pomace is approximately 17.43% at the end of analysis at 900°C (Figure 18).

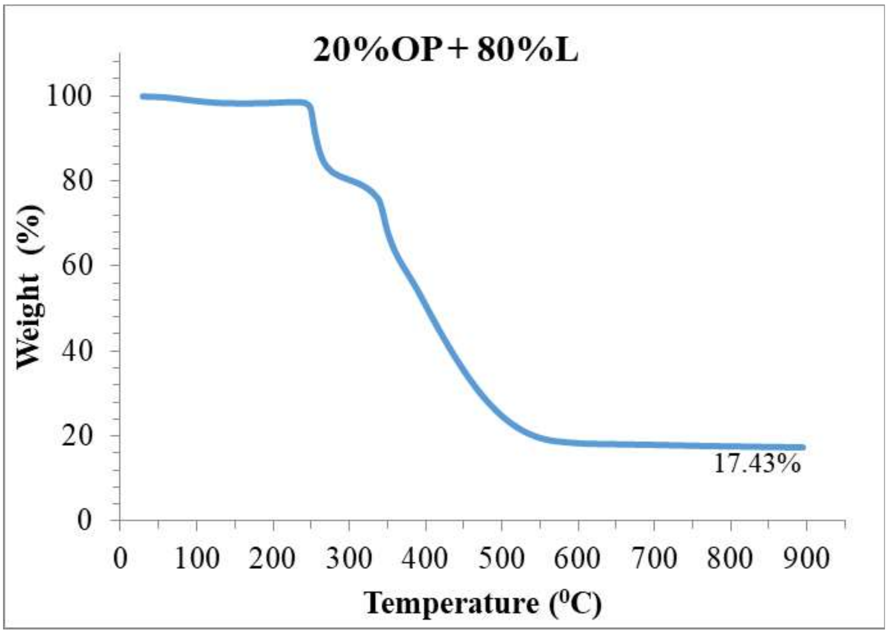


Figure 18. Thermogravimetry profile of the mixture containing 20% by weight of olive pomace

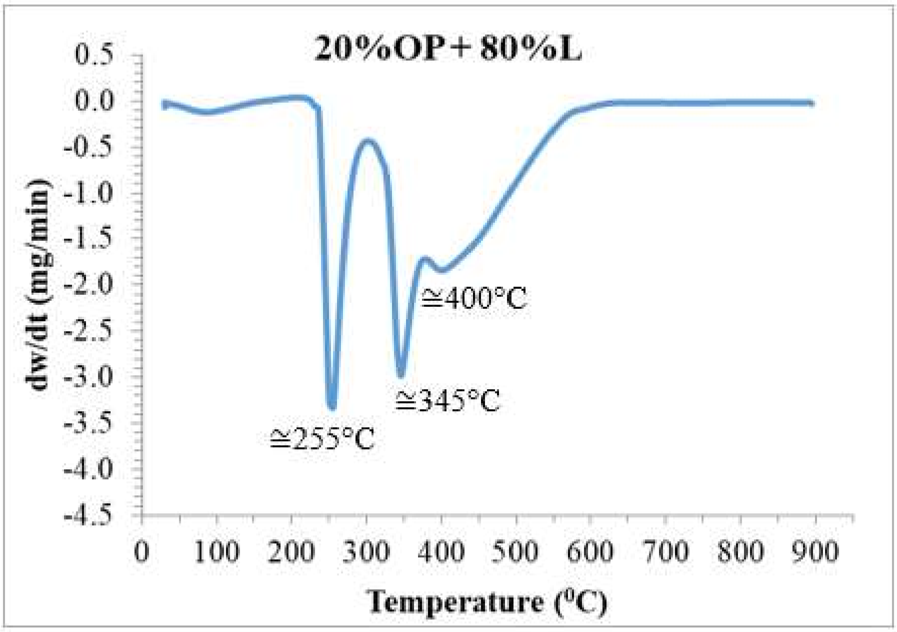


Figure 19. Differential Thermogravimetry profile of the mixture containing 20% by weight of olive pomace

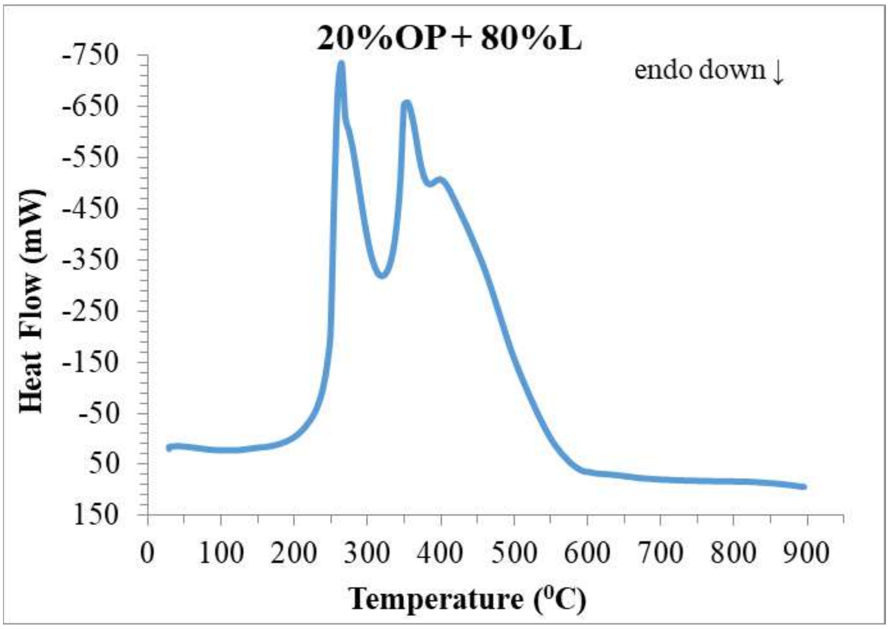


Figure 20. Differential Scanning Calorimeter profile of the mixture containing 20% by weight of olive pomace

TG and DTG profiles of blends containing 30% by weight of olive pomace are shown in Figure 21 and 22, DSC profile of same sample is shown in Figure 23. In TG profile, as in the previous samples, after moisture loss region, three weight loss regions were clearly observed (Figure 22). These regions are the temperature ranges of exothermic combustion reactions (Figure 23). The peak temperature of the first combustion region is observed approximately at 260°C, the peak temperature of the second region is observed approximately at 350°C and the peak temperature of third region is observed approximately at 405°C (Figure 23). When the profiles belonging to the sample containing 30% olive pomace are compared with the blends with 20% olive pomace, the intensity of the first and second combustion regions are seen to have increased. The amount of remaining materials of blends containing 30% by weight of olive pomace is approximately 15.45% at the end of analysis at 900 °C (Figure 21).

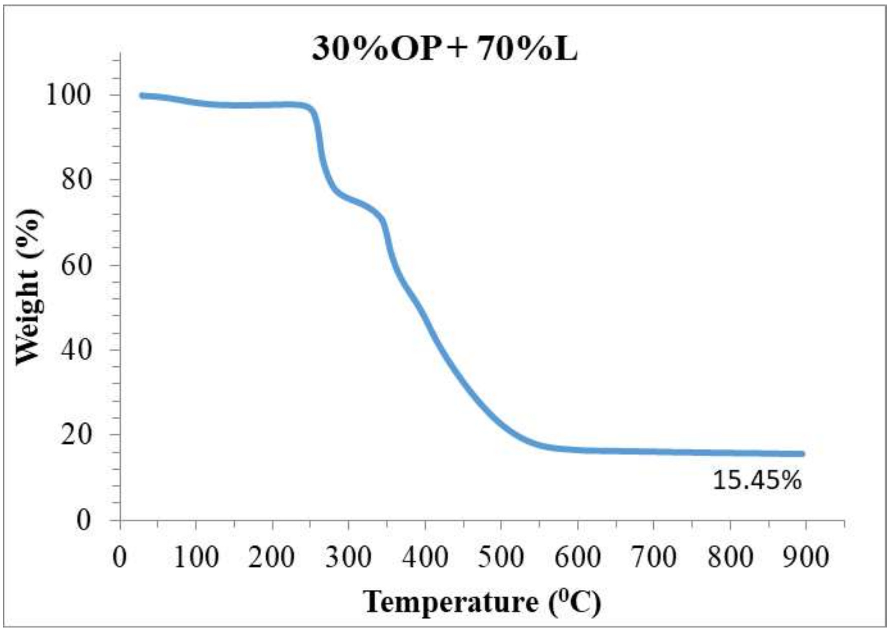


Figure 21. Thermogravimetry profile of the mixture containing 30% by weight of olive pomace

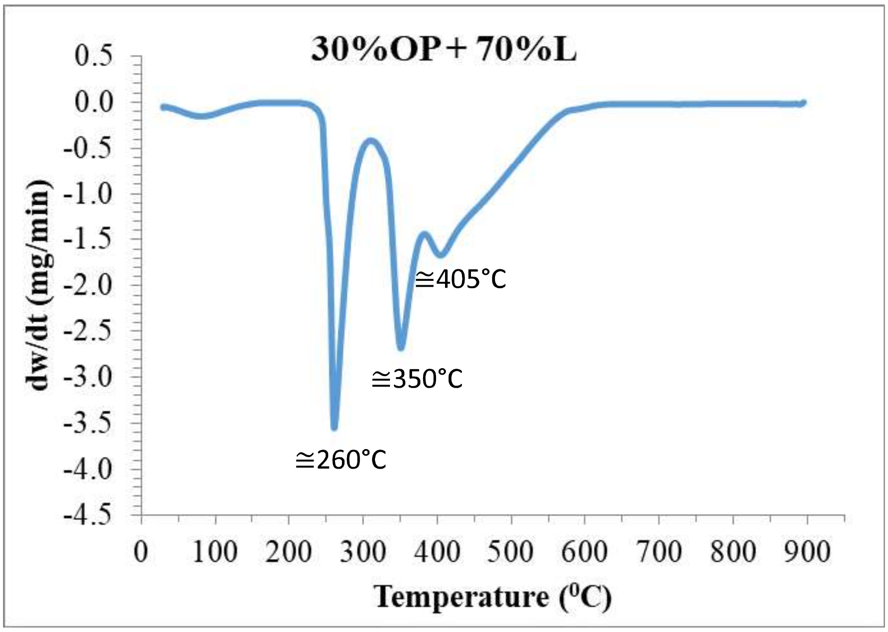


Figure 22. Differential Thermogravimetry profile of the mixture containing 30% by weight of olive pomace

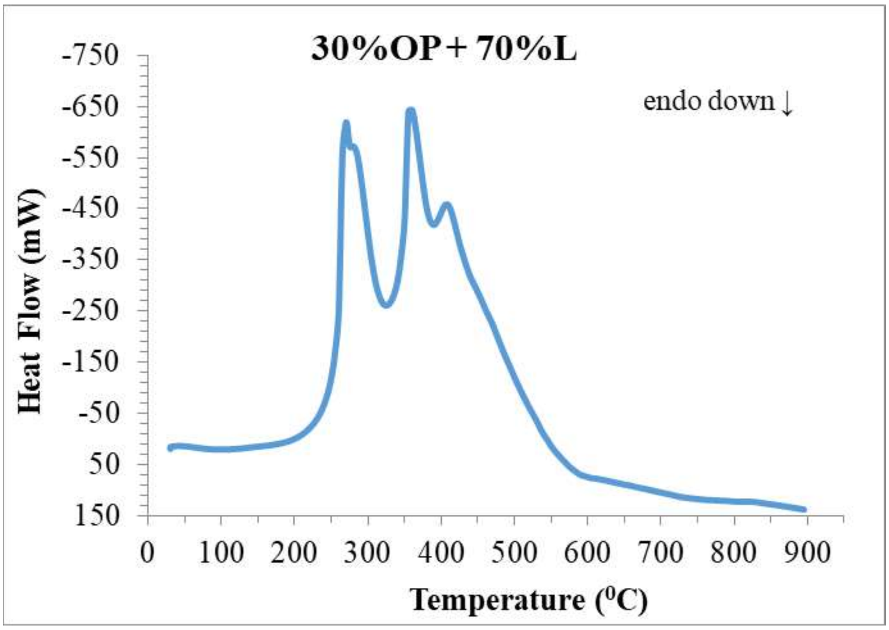


Figure 23. Differential Scanning Calorimeter profile of the mixture containing 30% by weight of olive pomace

TG and DTG profiles of blends containing 40% by weight of olive pomace are shown in Figure 24 and 25, DSC profile of same sample is shown in Figure 26. In DTG profile, as in the previous samples, after moisture loss region, three weight loss regions were clearly observed (Figure 25). These regions are the temperature ranges of exothermic combustion reactions (Figure 26). The peak temperature of the first combustion region is observed approximately as 260°C, the peak temperature of the second region is observed approximately as 350°C and the peak temperature of third region is observed approximately as 405°C (Figure 25). When the profiles belonging to the sample containing 40% olive pomace are compared with the blends with lower ratio of olive pomace, the intensity of the first combustion regions are seen to take place much more. The amount of remaining materials of blends containing 40% by weight of olive pomace is approximately 13.55% at the end of analysis at 900°C (Figure 24).

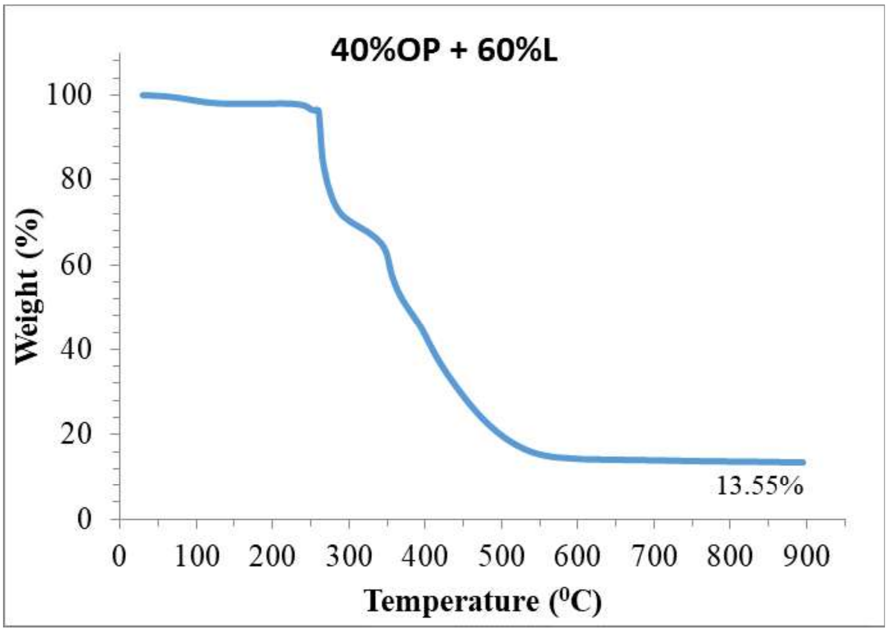


Figure 24. Thermogravimetry profile of the mixture containing 40% by weight of olive pomace

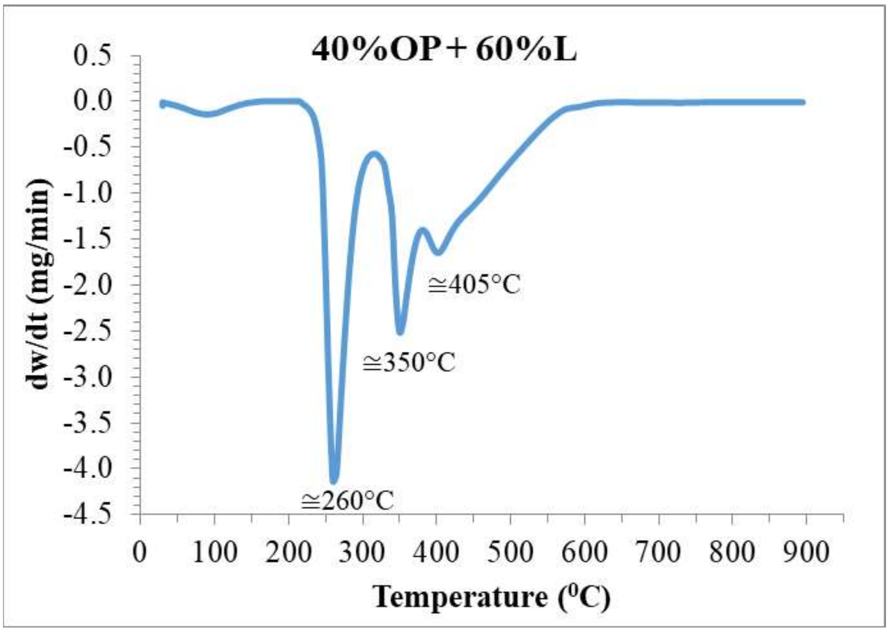


Figure 25. Differential Thermogravimetry profile of the mixture containing 40% by weight of olive pomace

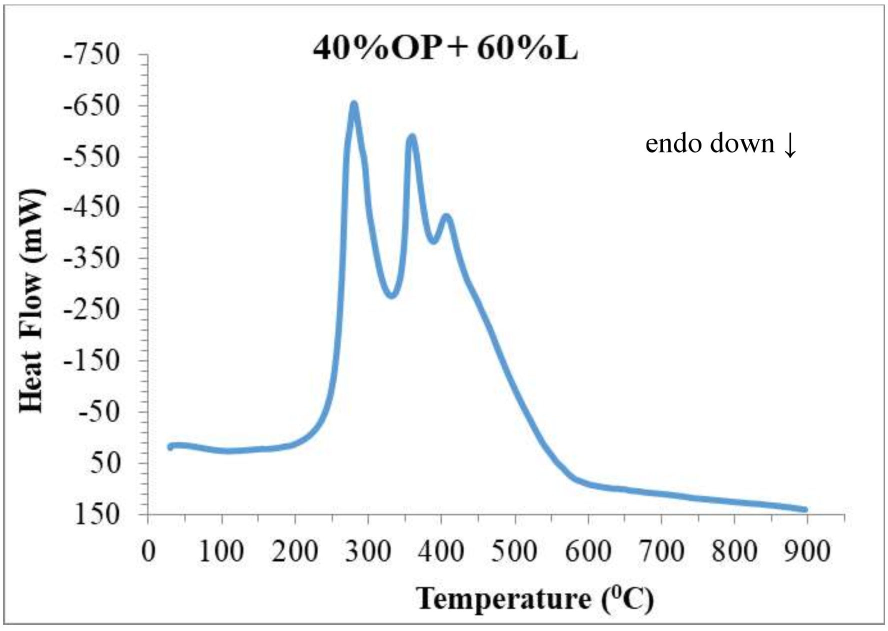


Figure 26. Differential Scanning Calorimeter profile of the mixture containing 40% by weight of olive pomace

TG and DTG profiles of blends containing 50% by weight of olive pomace are shown in Figure 27 and 28, DSC profile of same sample is shown in Figure 29. In DTG profile, as in the previous samples, after moisture loss region, three weight loss regions were clearly observed (Figure 28). These regions are the temperature ranges of exothermic combustion reactions (Figure 29). The peak temperature of the first combustion region is observed approximately as 270°C, the peak temperature of the second region is observed approximately as 365°C and the peak temperature of third region is observed approximately as 415°C (Figure 28). When the profiles belonging to the sample containing 50% olive pomace are compared with run-of-mine lignite sample and the blends with lower ratio of olive pomace, the intensity of the first combustion regions are seen to take place much more and intensity of the second combustion region are seen to increase. The amount of remaining materials of blends containing 50% by weight of olive pomace is approximately 11.76% at the end of analysis at 900°C (Figure 27).

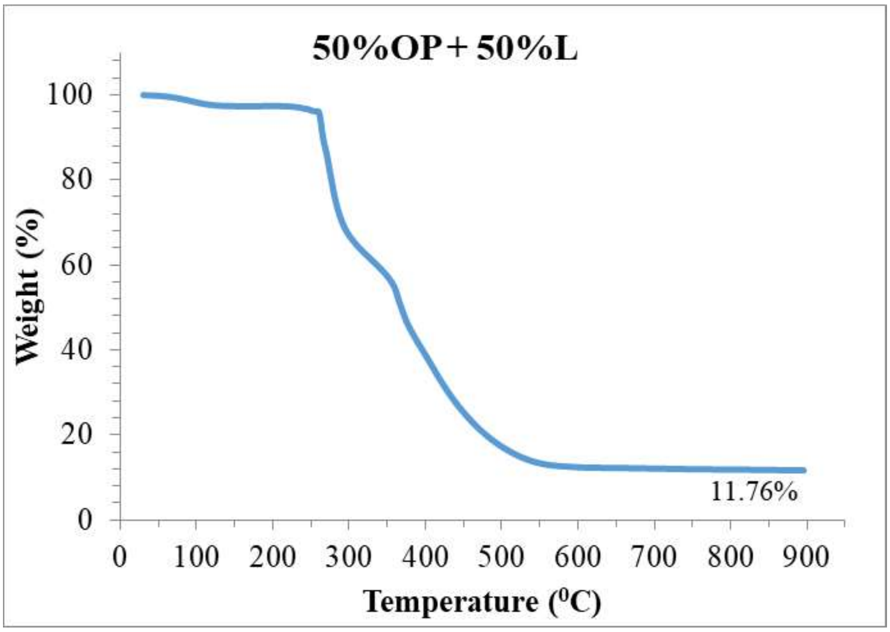


Figure 27. Thermogravimetry profile of the mixture containing 50% by weight of olive pomace

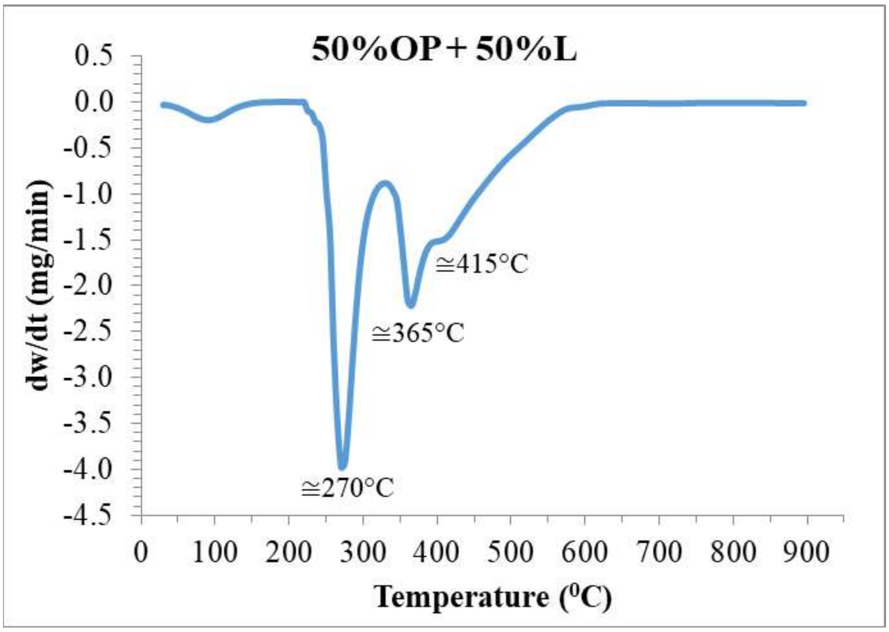


Figure 28. Differential Thermogravimetry profile of the mixture containing 50% by weight of olive pomace

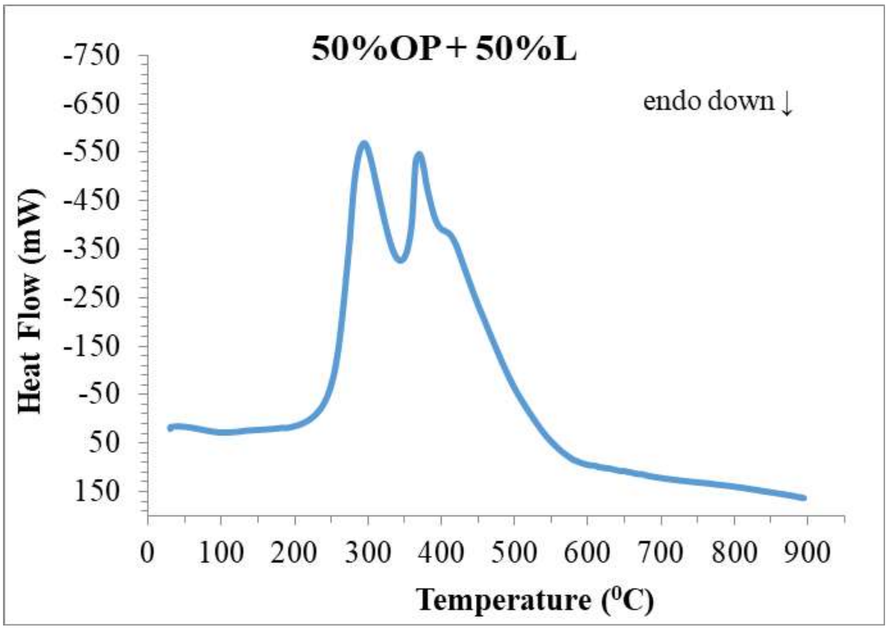


Figure 29. Differential Scanning Calorimeter profile of the mixture containing 50% by weight of olive pomace

The main data values after combustion of the lignite, olive pomace, and olive pomace-lignite blends are shown in Table 7. The characteristics of the thermal behavior of the olive pomace-lignite blends are shown in Table 8. As seen in TG/DTG and DSC profiles, the main combustion regions for all mixtures are first and second regions. Table 7 shows that amount of material remaining after combustion of lignite (20.21%) is the highest, in other words, weight losses are lowest value compared to the weight losses of olive pomace and blends. Moreover, in terms of olive pomace, amount of material remaining after combustion of olive pomace (0.91%) is the lowest value, in other words, weight losses are the highest value compared to the weight losses of lignite and blends. In terms of olive pomace-lignite blends, when the results were evaluated together, it was determined that the peak temperature of the first and second combustion regions tend to shift to higher temperature depending on the addition rate of olive pomace in the mixture. When the addition rate of olive pomace is increased from 10% to 50%, the amount of remaining material at the end of the reaction decreases significantly and decreases from 19% to 11.76% (Table 7). The increase in the ratio of olive pomace causes an increase in the speed of weight loss and heat flow in both first and second regions. The DTG and DSC data recorded at the peak temperatures of the first and second regions clearly show this increase. These increases are higher for the first reaction region (Table 8). This shows that the increase in addition rate of olive pomace increases the intensity of combustion in both regions but contributes more to the intensity of first reaction. In summary, it can be said that the combustion efficiency of the hybrid olive pomace- lignite fuel is much higher than that of lignite either higher heat flow values or lower amount of material remaining at the end of the reaction.

Table 7. The peak temperatures of the combustion regions of lignite, olive pomace and olive pomace-lignite blends and amount of material remaining after combustion

Blends	1st Peak Temperature °C	2nd Peak Temperature °C	3rd Peak Temperature °C	Amount of Material Remaining %
Lignite	272.5	377.5	422.5	20.21
10%OP + 90%L	255	345	395	19.00
20%OP + 80%L	255	345	400	17.43
30%OP + 70%L	260	350	405	15.45
40%OP + 60%L	260	350	405	13.55
50%OP + 50%L	270	365	415	11.76
Olive Pomace	270	345	430	0.91

Table 8. Thermal characteristics of the main combustion regions of olive pomace-lignite blends

Blends	1st Region			2nd Region		
	Peak Temperature (°C)	dw/dt* (mg/min)	Heat Flow** (mW)	Peak Temperature (°C)	dw/dt* (mg/min)	Heat Flow** (mW)
10%OP + 90%L	255	-2.12	-580.61	345	-2.42	-579.83
20%OP + 80%L	255	-3.01	-605.75	345	-2.54	-590.13
30%OP + 70%L	260	-3.51	-642.76	405	-2.68	-606.85
40%OP + 60%L	260	-4.14	-685.34	405	-2.81	-619.54
50%OP + 50%L	270	-4.49	-745.08	415	-2.96	-638.13

*The increase in negative values corresponds to the increase in the rate of the instantaneous weight loss

**The increase in negative value corresponds to the intensity increase in exothermic reaction and the increase in heat released

Table 9. Thermal values of olive pomace-lignite blends and Sulfur content

Blends	Lower Calorific Value (kCal/kg) as received basis	Moisture (%)	Total Sulfur Amount (%)	
			As received basis	Dry basis
10%OP + 90%L	5512.58	6.97	2.18	2.34
20%OP + 80%L	5442.16	7.6	1.9	2.06
30%OP + 70%L	5290.78	8.2	1.67	1.82
40%OP + 60%L	5238.56	8.62	1.48	1.62
50%OP + 50%L	5102.24	9.32	1.25	1.38

In addition to thermal analyses of the blends, the thermal value and total sulfur content, which are important criteria in their marketing, were also evaluated. Table 9 shows the lower calorific value and total sulfur values for mixtures containing different proportions of olive pomace by weight. The evaluation of the availability of solid fuels is based on the lower calorific value on the received base and the sulfur content is generally considered on a dry basis. Therefore, the thermal values of the mixtures are given on the received basis and the total sulfur content is given on both the received and dry basis. As it can be seen in Table 9, the lower calorific value of the all mixtures remain above the range of 5100 kCal/kg. In terms of sulfur, the total sulfur content of the mixture containing 10% olive pomace is only slightly above 2.3% and below 20% olive pomace addition, it can decrease to levels about 2%. Accordingly, all mixtures in terms of the lower calorific value and especially mixtures of 20% and higher olive pomace amount in terms of the total sulfur content are rehabilitated fuel. It is clear that lignite sample with Sulfur content of 2.64% as dry basis cannot be used for the purpose of heating without a cleaning process of the sulfur content. Therefore, the degree and importance of this rehabilitation obtained with the contribution of addition of olive pomace was better understood without any treatment of lignite.

6.3. Investigation of Tendency to Combustion of Lignite and Olive Pomace

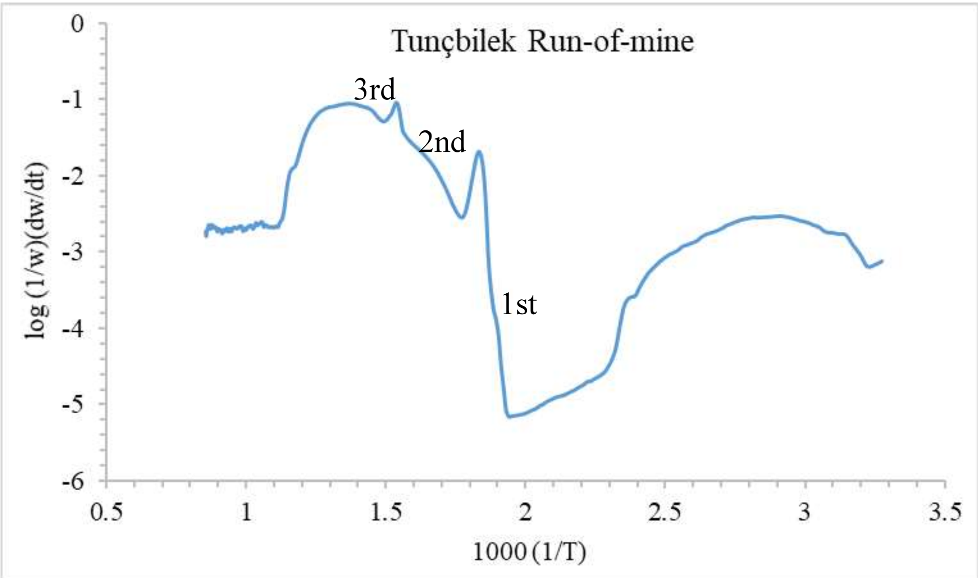
One of the most important criteria observed in the study regarding the combustion characteristics and tendency to combustion is considered in decrease in the activation energies of the fuels.

For any fuel, there are many studies (Altun et al., 2006) in the literature that investigate the tendency to combustion which is directly related to the activation, increase in activation energy and/or high activation energies are negative situation in terms of tendency to combustion, and any decrease in the activation energy resulting from any process corresponds to an increase in the tendency of the fuel to burn, meaning that the combustion characteristics are improved.

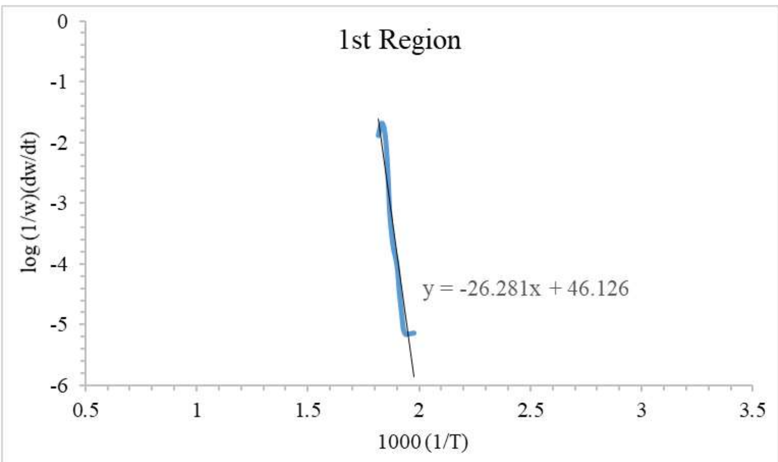
In order to evaluate the tendency of olive pomace-lignite blends to combustion, firstly, samples of R.O.M lignite and olive pomace were studied separately and individually. As mentioned earlier in the study, in order to calculate kinetic analyses and activation energies for the evaluation of tendency to Tunçbilek lignite combustion and olive pomace, Arrhenius Model- Weighted Average Activation Energy Approach was applied on TG/DTG data. Activation energies were determined for lignite and olive pomace samples individually and then for mixtures of lignite and olive pomace in varying proportions and evaluated comparatively.

Figure 30 shows the graphs obtained from the application of Arrhenius Model to the DTG data of Tunçbilek lignite. Three independent exothermic combustion regions were determined by taking into account DTG and DSC profiles of the R.O.M lignite sample. These regions and the application of Arrhenius model to these regions are also shown in Figure 30. At the same time, regional weight losses were determined from the DTG data and the activation energies were calculated for each reaction region. It should be noted that here the activation energies are only calculated for the combustion regions of exothermic properties. Therefore, weight loss region (Figure 10), in the DTG profile of Tunçbilek lignite, where occurring moisture loss and does not have exothermic property, is not taken into account when calculating the activation energy that reflects the tendency of the fuel to burn.

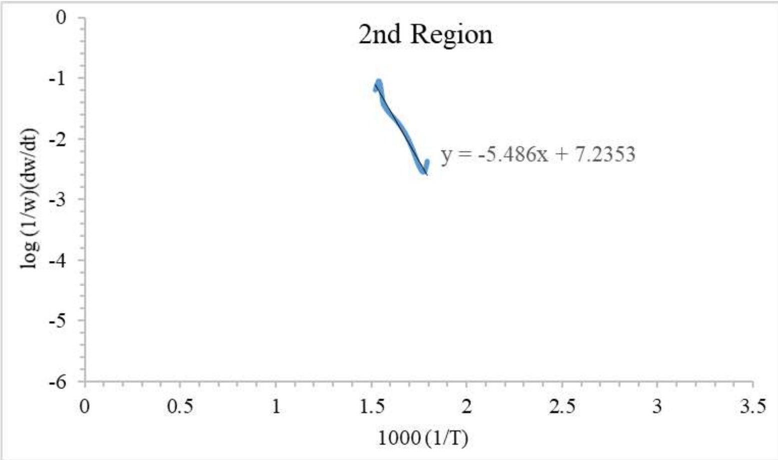
Activation energies for exothermic regions where combustion occurs for Tunçbilek coal are 5.63 kJ/mol for 1st region, 17.88 kJ/mol for 2nd region, and 8.88 kJ/mol for 3rd region and cumulative activation energy (E_{wm}) corresponds to 32.39 kJ/mol. Although the slope of the Arrhenius line obtained for the 1st region is higher than both 2nd and 3rd regions, the weight losses in the 2nd and 3rd regions are much higher than the 1st region, and the activation energy values of the 2nd and 3rd are higher than 1st region.



a)



b)

c) 

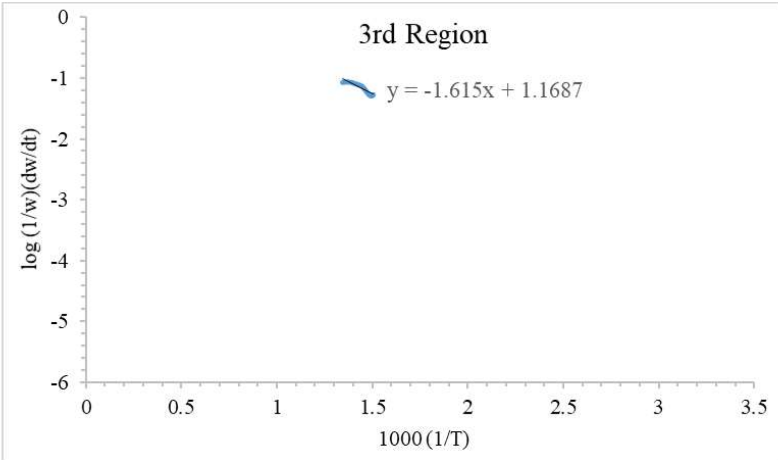
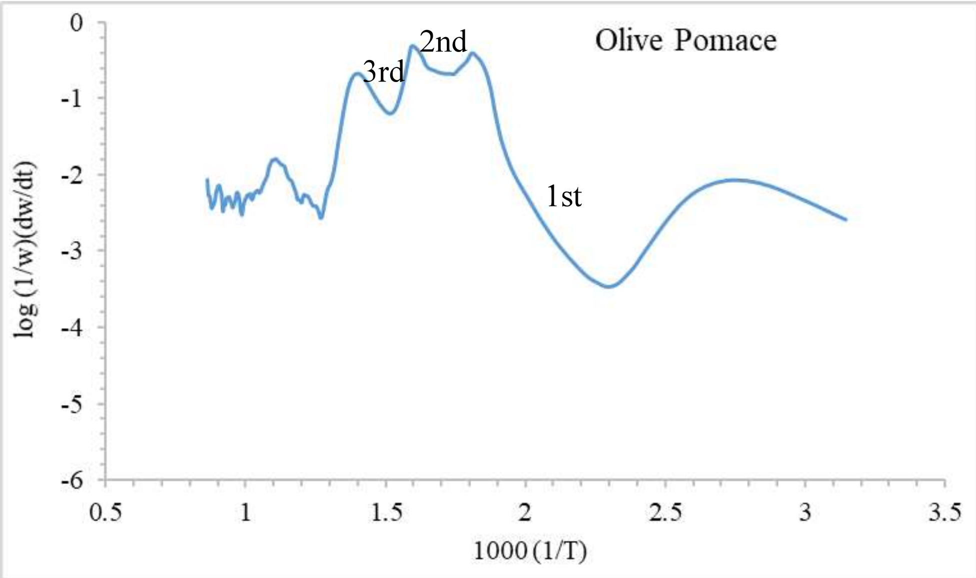
d) 

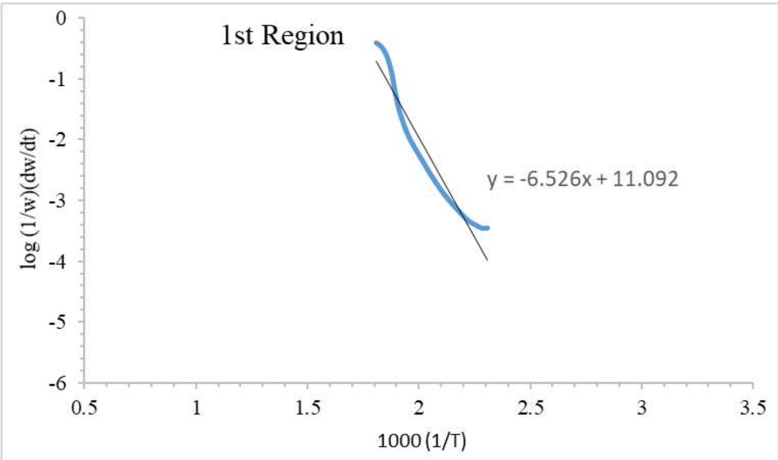
Figure 30. Result of application of Arrhenius Kinetic Model to lignite sample(a) and exothermic regions (b, c, d)

Based on the DTG and DSC profiles of the olive pomace sample, three independent exothermic combustion regions were determined and these regions and application of Arrhenius model to these regions are shown in Figure 31. For each exothermic combustion region, regional weight losses obtained from the DTG data were determined and the activation energies for each reaction region were calculated. Parallel to the DTG profile of the olive pomace different than lignite, the profile used in the application of the Arrhenius model is quite different (Figure 10 and 13). The 1st region, where combustion occurs, covers a much wider temperature range than the 2nd

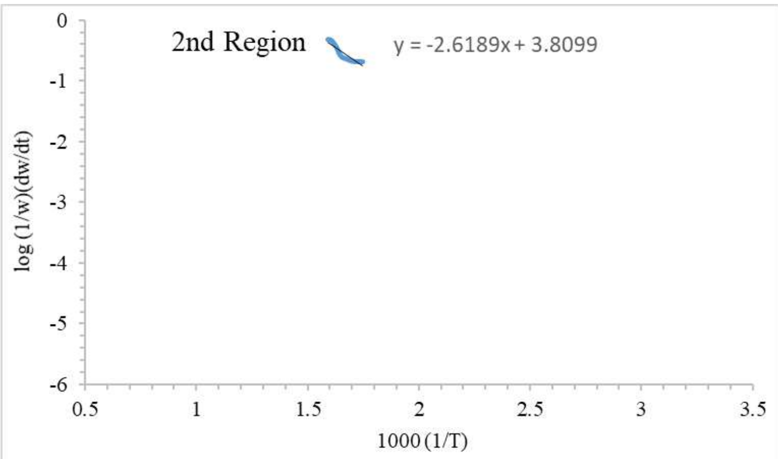
and 3rd combustion regions. This region, is also the range where the highest weight loss occurs, is the main combustion region in the thermal behavior of olive pomace. Activation energies in exothermic regions where combustion occurs; 69.22 kJ/mol for 1st region, 12.07 kJ/mol for 2nd region, 1.83 kJ/mol for 3rd region and cumulative activation energy (E_{wm}) corresponds to 83.12 kJ/mol. Since the slope of the Arrhenius line obtained for the 1st region is higher than the 2nd and 3rd regions and the weight loss in this region is quite high compared to the other two regions, the activation energy value obtained for the 1st region is much higher than the activation energy values of the other two regions. The activation values obtained for olive pomace and lignite samples indicate that these two fuels differ in their tendency to burn. The region with the highest activation energy between the three different combustion regions observed in Tunçbilek lignite is the 2nd region. This region, is also the region where the highest weight loss occurs between the combustion regions, in other words the highest amount of organic material is oxidized, and is the main combustion region. For olive pomace, three different combustion regions were observed but the highest activation energy was determined for the 1st region. As mentioned above, the activation energy value for 1st region is quite high compared to the other combustion regions. This results from both the steep slope of the Arrhenius line (high slope) and the high weight loss in this region. In other words, although the main combustion region for Tunçbilek lignite is the narrow range of about 340 – 365°C, the main combustion region in the olive pomace sample corresponds to a more severe combustion reaction at a lower and wider temperature range (270 - 335°C).

a)


Olive Pomace
3rd
2nd
1st
log (1/w)(dw/dt)
1000 (1/T)
0
-1
-2
-3
-4
-5
-6
0.5
1
1.5
2
2.5
3
3.5

b)


1st Region
y = -6.526x + 11.092
log (1/w)(dw/dt)
1000 (1/T)
0
-1
-2
-3
-4
-5
-6
0.5
1
1.5
2
2.5
3
3.5

c)


2nd Region
y = -2.6189x + 3.8099
log (1/w)(dw/dt)
1000 (1/T)
0
-1
-2
-3
-4
-5
-6
0.5
1
1.5
2
2.5
3
3.5

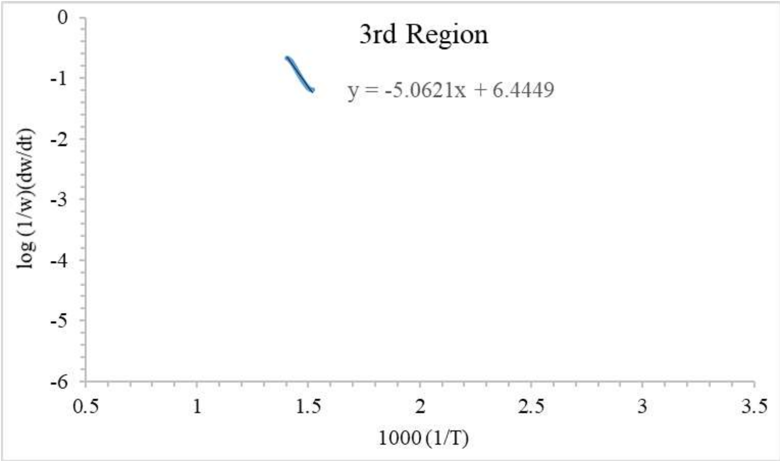
d) 

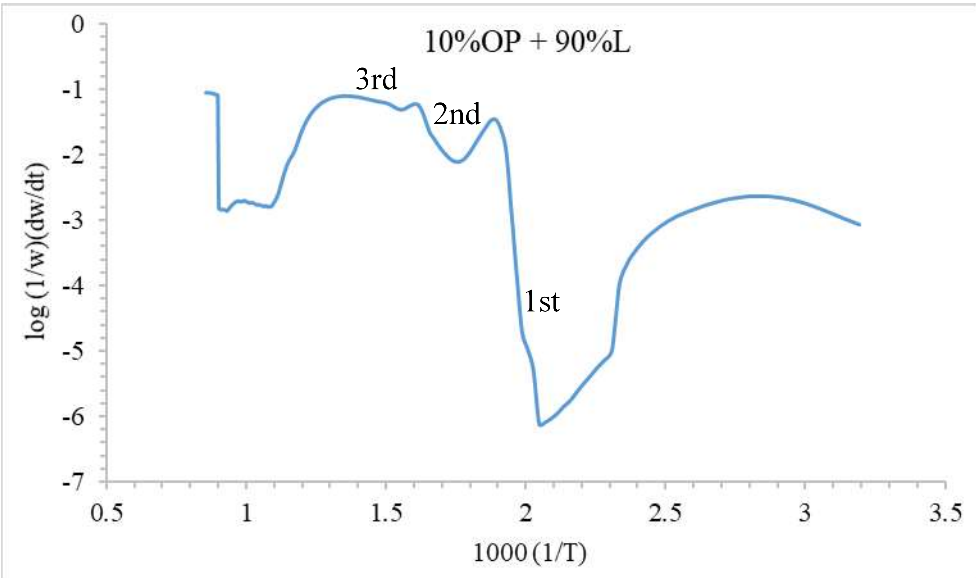
Figure 31.Result of application of Arrhenius Kinetic Model to olive pomace sample(a) and exothermic regions (b, c, d)

The activation energy (17.88 kJ/mol) obtained for the main combustion region and the cumulative activation energy (32.39 kJ/mol) for Tunçbilek lignite is quite lower than the activation energy (69.22 kJ/mol) obtained for the main combustion region and the cumulative activation energy (83.12 kJ/mol) for olive pomace. This shows that olive pomace, which has better properties than lignite in terms of inorganic content, calorific value and calorimetric profile, has lower tendency to combustion than lignite. In other words, lignite is more prone to ignition and combustion reaction. Therefore, the hybrid-fuel approach with this study supports the hypothesis that these two fuels can effectively rehabilitate the negative characteristics of each other, that is rather than using these two fuels alone, they can give more effective results.

6.4. Investigation of the Combustion of Lignite and Olive Pomace Blends-Kinetic Analysis

The application of the Arrhenius model to the TG / DTG data of the mixture containing 10% of olive pomace and 90% of Tunçbilek lignite by weight is shown in Figure 32. When the DTG and DSC profiles of the mixture were taken into consideration, three independent exothermic combustion regions were determined. As in the case of lignite and olive pomace samples, regional weight losses obtained from the DTG data for each exothermic combustion regions were determined in the fuel mixtures and the activation energies for each reaction region were calculated.

Activation energies in exothermic regions where combustion occurs; 23.62 kJ/mol for 1st region, 7.81 kJ/mol for 2nd region, 5.25 kJ/mol for 3rd region and cumulative activation energy (E_{wm}) corresponds to 36.68 kJ/mol. Since the slope of Arrhenius line obtained for the 1st region is higher than the 2nd and 3rd regions and the weight loss in this region is quite high compared to the other two regions, the activation energy value obtained for the 1st region is above the activation energy values of the other two regions. Furthermore, the main combustion region for the mixture is the 1st region. Another point is that the cumulative activation energy of the olive pomace-lignite mixture is higher than that of rom lignite and lower than that of the olive pomace. In addition, addition of olive pomace, even at 10%, is sufficient to differentiate the combustion behavior and tendency to burn of lignite. One of the most important differences is, with addition of olive pomace, reduction of efficiency of 2nd region and to become the main combustion region of the 1st region (Figure 32).



a)

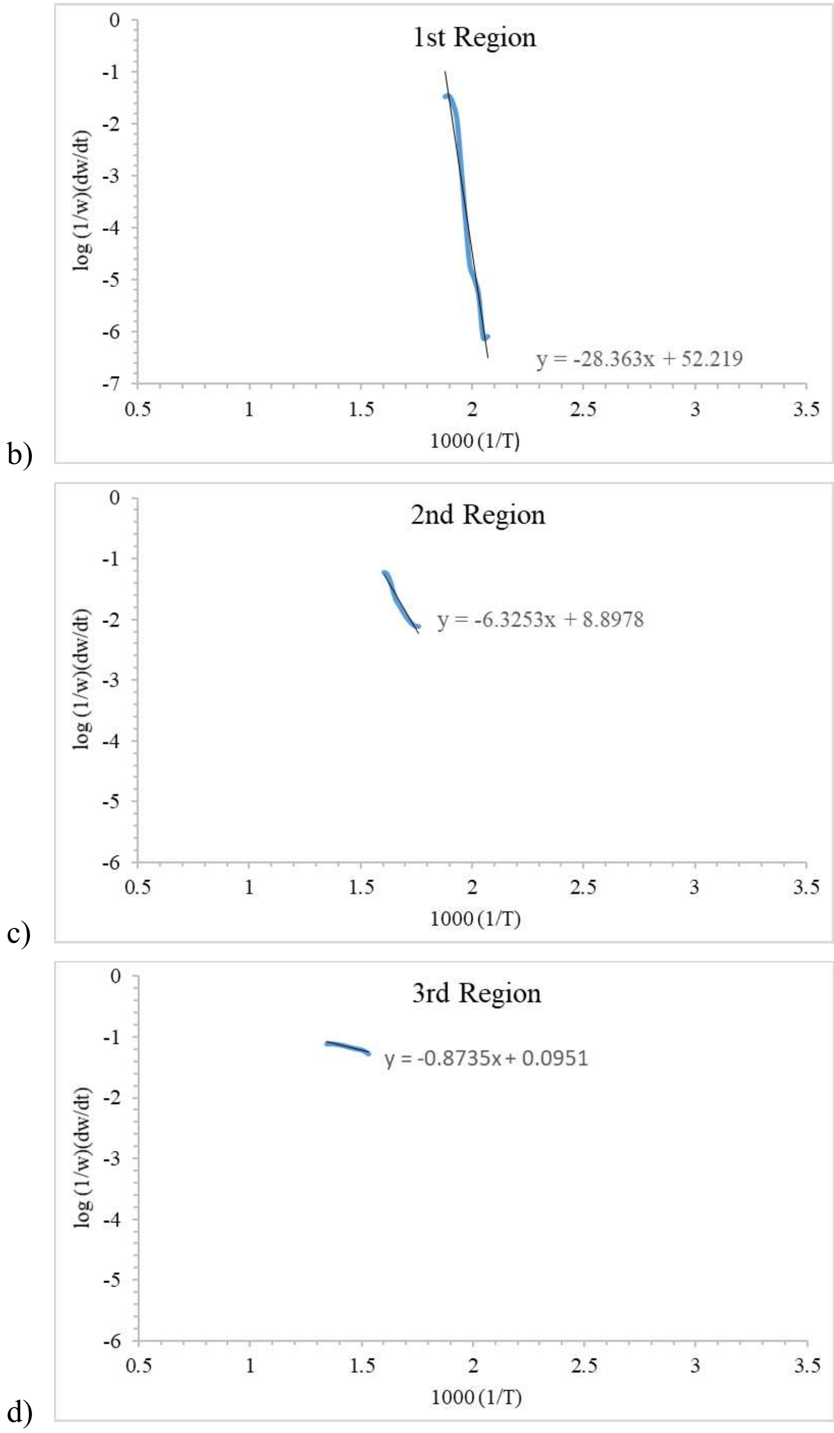
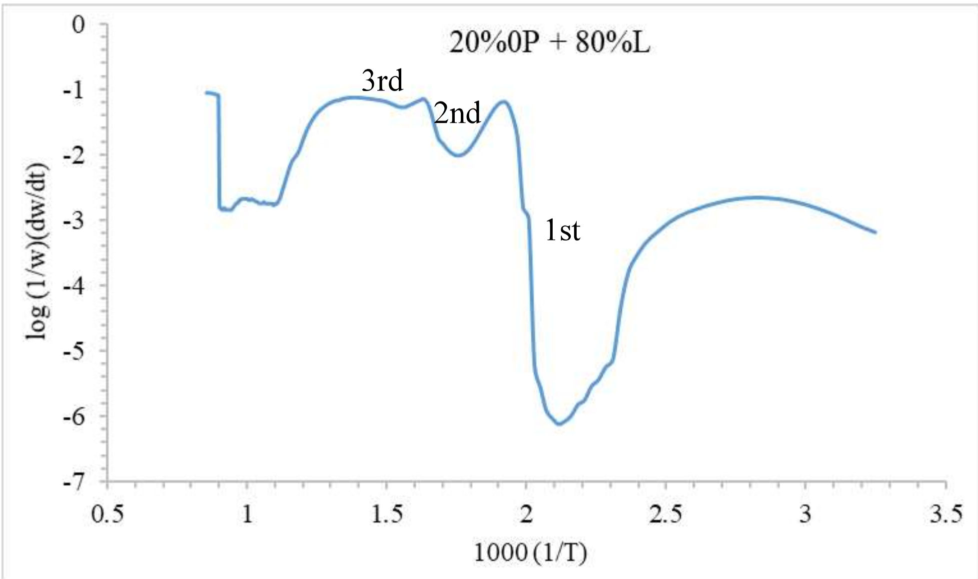
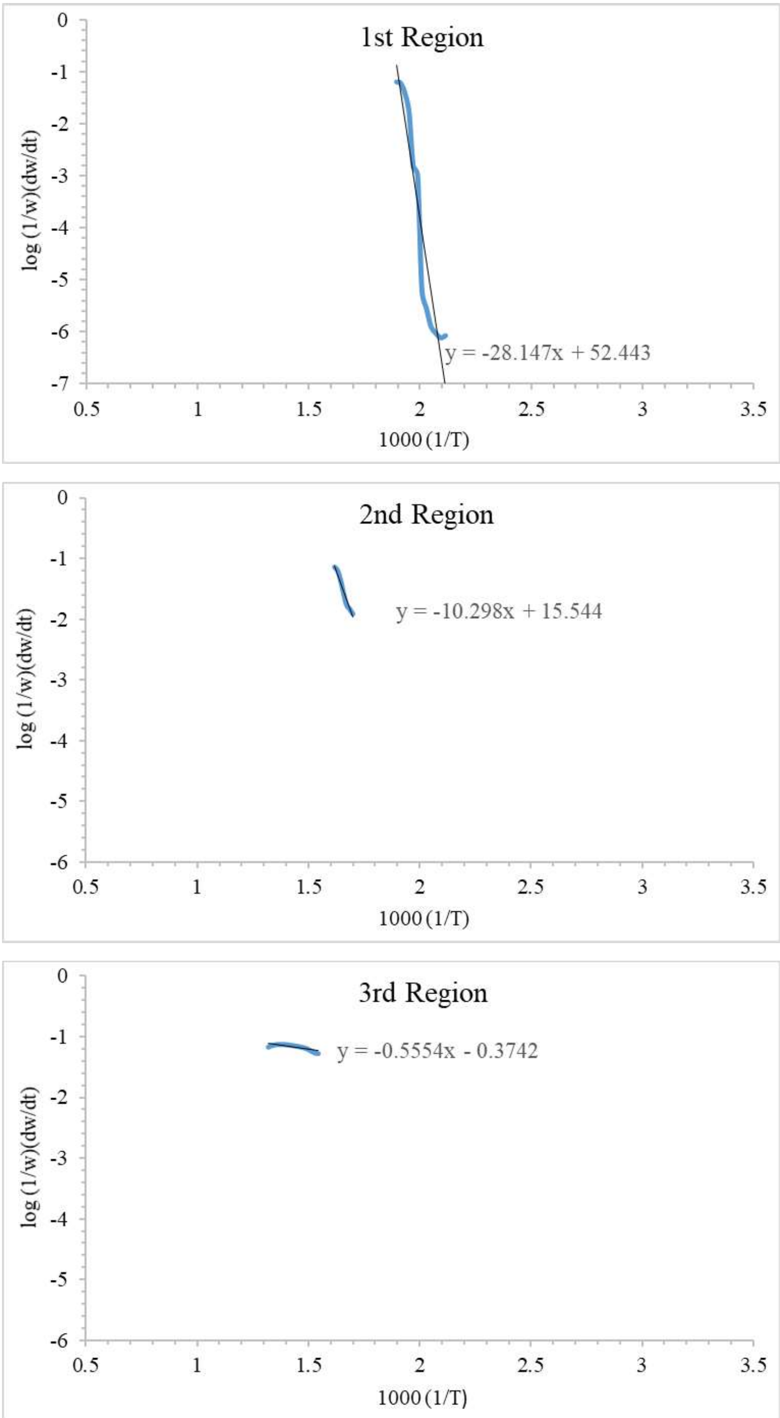


Figure 32. Results of application of Arrhenius Kinetic Model to the mixture containing 10% of olive pomace by weight(a) and exothermic regions (b, c, d)

The application of the Arrhenius model to the TG / DTG data of the mixture containing 20% of olive pomace and 80% of Tunçbilek lignite by weight is shown in Figure 33. When the DTG and DSC profiles of the mixture were taken into consideration, three independent exothermic combustion regions were determined. Activation energies in exothermic regions where combustion occurs; 27.66 kJ/mol for 1st region, 8.91 kJ/mol for 2nd region, 3.21 kJ/mol for 3rd region and the cumulative activation energy (E_{wm}) corresponds to 39.78 kJ/mol. The main combustion region for the mixture containing 20% of olive pomace is the 1st region. In addition, as the ratio of the olive pomace in the mixture increases, the activation energy of the 1st and 2nd combustion regions increase and the activation energy of the 3rd region decreases.



a)



b)

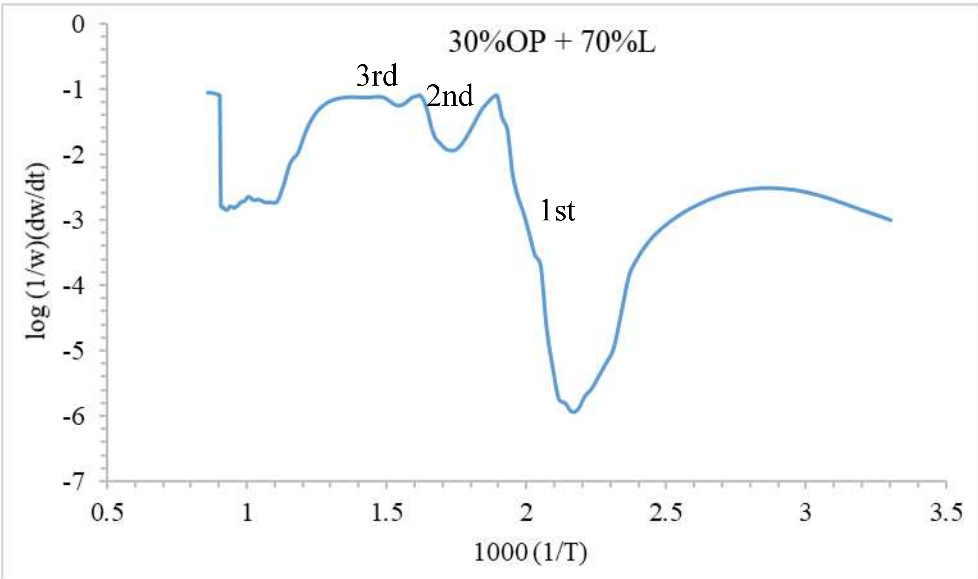
c)

d)

Figure 33.Results of application of Arrhenius Kinetic Model to the mixture containing 20% of olive pomace by weight (a) and exothermic regions (b, c, d)

The application of the Arrhenius model to the TG / DTG data of the mixture containing 30% of olive pomace and 70% of Tunçbilek lignite by weight is shown in Figure 34. When the DTG and DSC profiles of the mixture were taken into consideration, three independent exothermic combustion regions were determined. Activation energies in exothermic regions where combustion occurs; 30.50 kJ/mol for 1st region, 10.60 kJ/mol for 2nd region, 2.80 kJ/mol for 3rd region and cumulative activation energy (E_{wm}) corresponds to 43.91 kJ/mol. The main combustion region for the mixture containing 30% of olive pomace is the 1st region. The activation energies of the 1st and 2nd combustion regions were increased by increasing the ratio of the olive pomace in the mixture from 20% to 30%, and the activation energy of 3rd region was continued to decrease.

a)



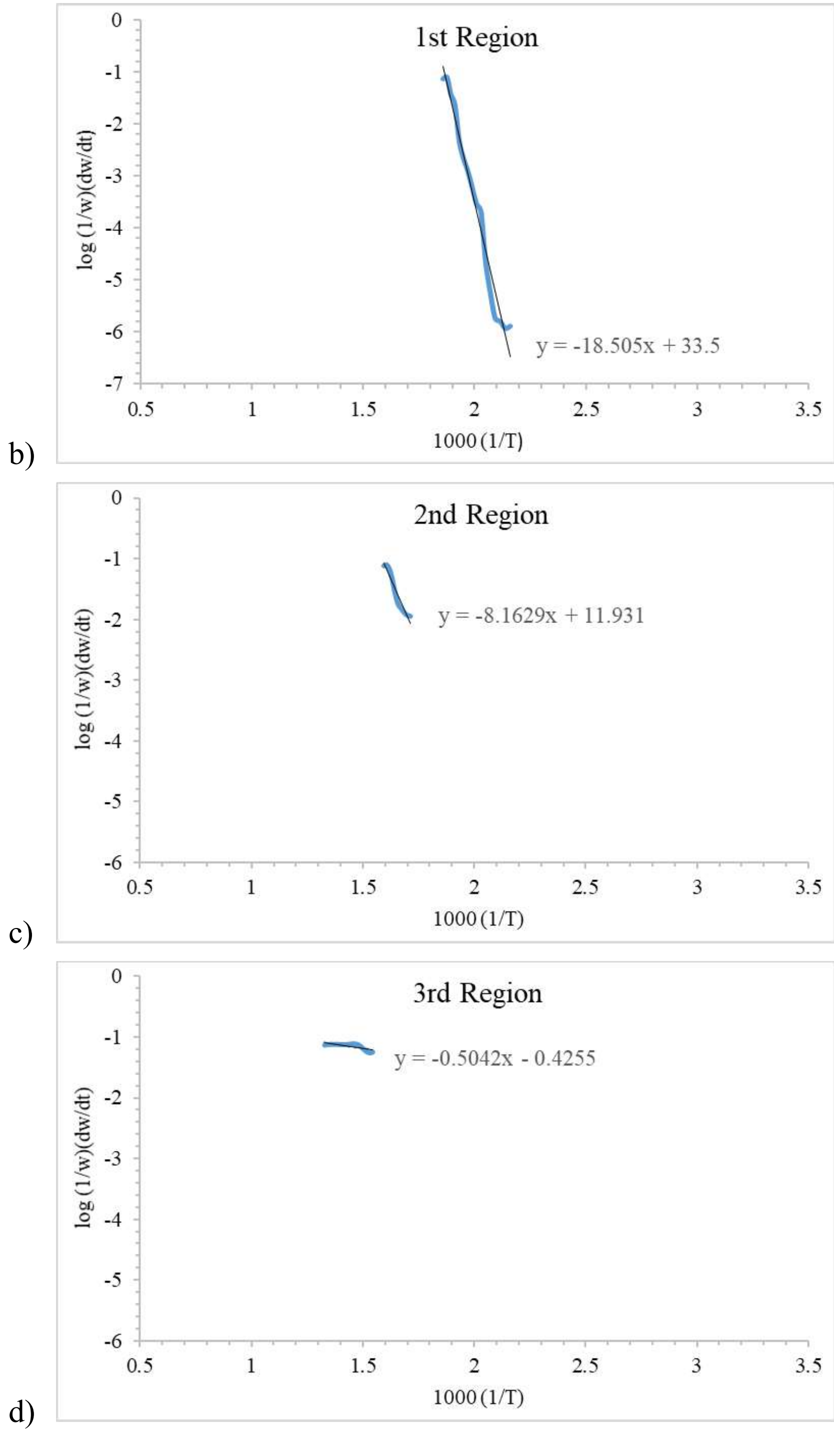
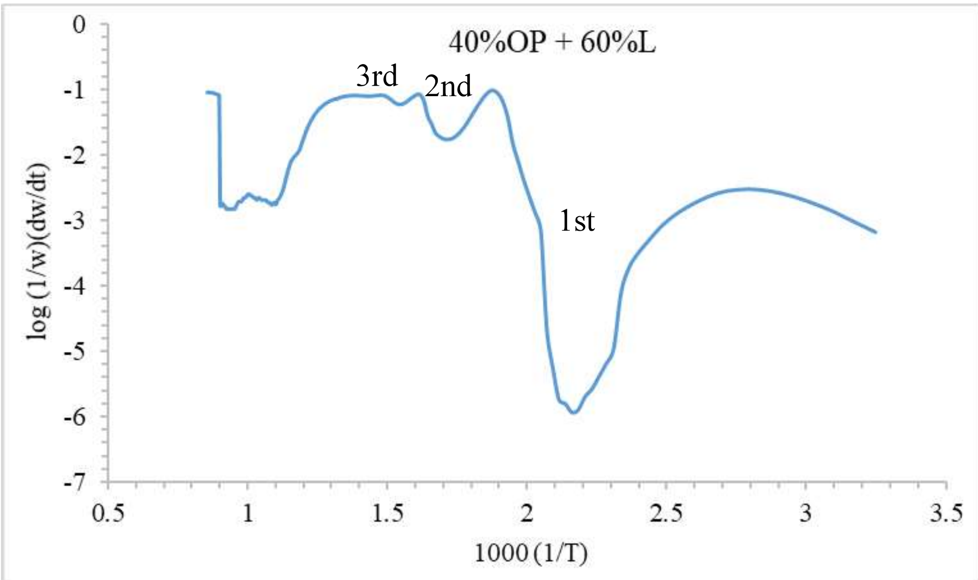
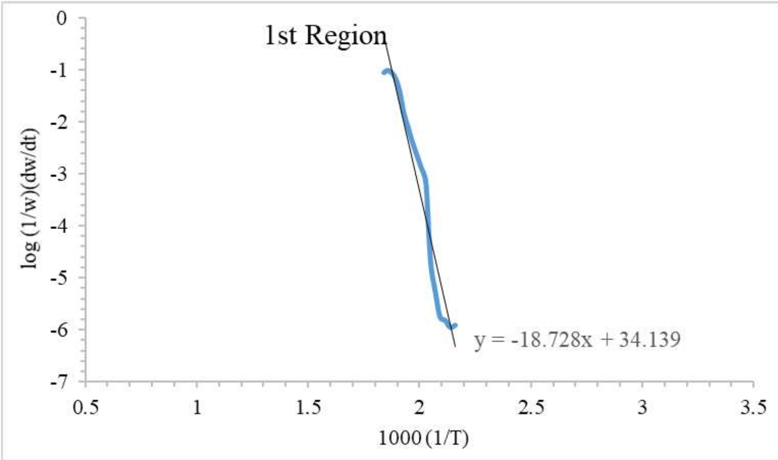


Figure 34. Results of application of Arrhenius Kinetic Model to the mixture containing 30% of olive pomace by weight (a) and exothermic regions (b, c, d)

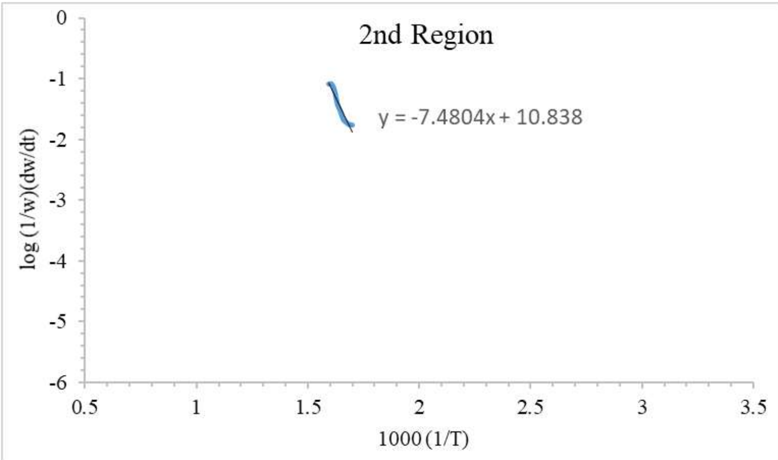
The application of the Arrhenius model to the TG / DTG data of the mixture containing 40% of olive pomace and 60% of Tunçbilek lignite by weight is shown in Figure 35. When the DTG and DSC profiles of the mixture were taken into consideration, three independent exothermic combustion regions were determined. Activation energies in exothermic regions where combustion occurs; 34.11 kJ/mol for 1st region, 13.01 kJ/mol for 2nd region, 1.93 kJ/mol for 3rd region and the cumulative activation energy (E_{mw}) corresponds to 49.05 kJ/mol. The main combustion region for the mixture containing 40% of olive pomace is the 1st region. The activation energies of the 1st and 2nd combustion regions were increased by increasing the ratio of the olive pomace in the mixture from 30% to 40%, and the activation energy of 3rd region was continued to decrease.



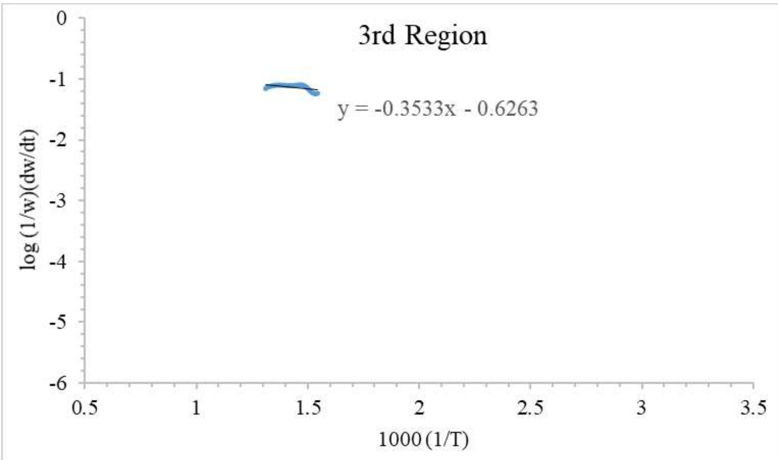
a)



b)



c)

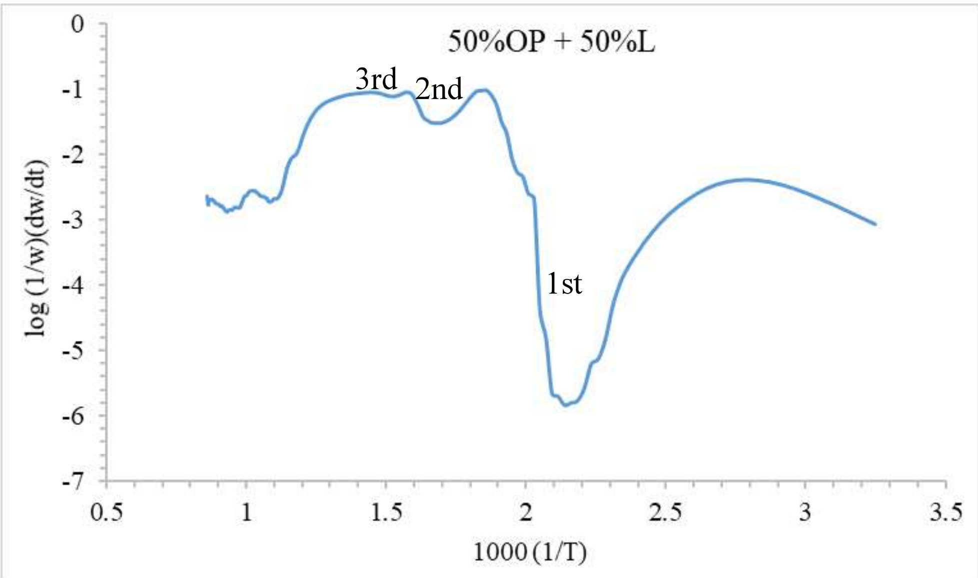


d)

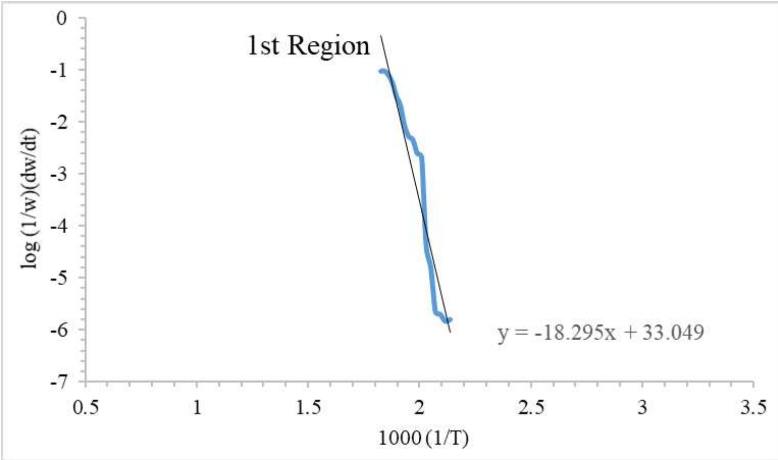
Figure 35. Results of application of Arrhenius Kinetic Model to the mixture containing 40% of olive pomace by weight (a) and exothermic regions (b, c, d)

The application of the Arrhenius model to the TG / DTG data of the mixture containing equal amount of olive pomace (50%) and Tunçbilek lignite (50%) by weight is shown in Figure 36. When the DTG and DSC profiles of the mixture were taken into consideration, three independent exothermic combustion regions were determined. Activation energies in exothermic regions where combustion occurs; 40.65 kJ/mol for 1st region, 15.81 kJ/mol for 2nd region, 0.41 kJ/mol for 3rd region and cumulative activation energy (E_{wm}) corresponds to 56.87 kJ/mol. By increasing the ratio of the olive pomace to 50%, the highest cumulative activation energy value was reached among the olive pomace-lignite mixtures. In addition, similar to the previous mixture ratios, the increase in the olive pomace ratio increases the activation energies of the 1st and 2nd combustion regions, and causes to decrease in the activation energy of the 3rd region. However, even at the ratio of 50% of olive pomace, the cumulative activation energy of the mixture containing 50% of olive pomace and lignite (56.87 kJ/mol) remains much lower than the cumulative activation energy of the olive pomace sample (83.12 kJ/mol).

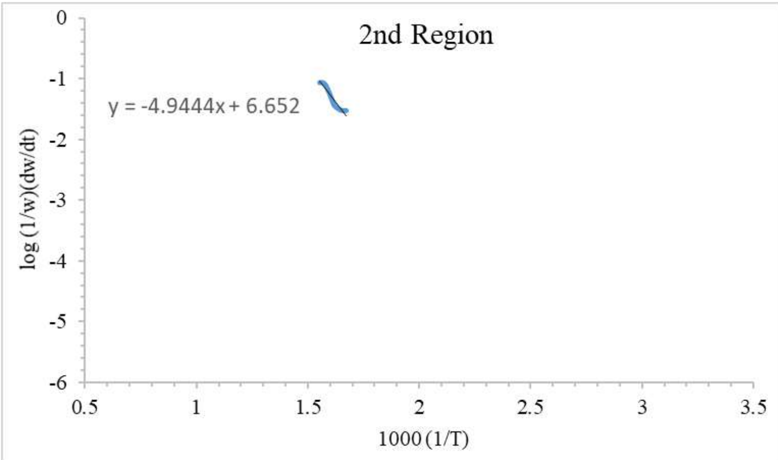
a)



b)



c)



d)

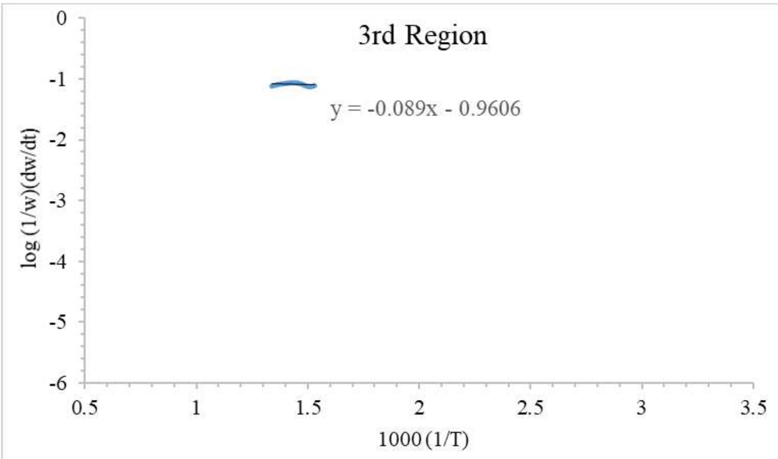


Figure 36.Results of application of Arrhenius Kinetic Model to the mixture containing 50% of olive pomace by weight (a) and exothermic regions (b, c, d)

Activation energy values obtained in different reaction regions for mixtures containing different proportions (10–50%) are observed in Table 10 also with the lignite and olive pomace values. When the reaction kinetics data obtained for the mixtures are evaluated together, it is seen that the cumulative activation energy values of all mixtures are much lower than activation energy value of olive pomace. This indicates that blends have more tendency to burn than olive pomace alone. In other words, as stated in the previous section, the presence of lignite in the mixture decreases the disadvantage of the olive pomace in terms of its combustion tendency and rehabilitates this negative feature of the olive pomace.

Table 10. Comparative representation of the activation energies of the lignite, olive pomace and olive pomace-lignite mixtures

	Activation Energy (kJ/mol)			
	1st region	**2nd region**	**3rd region**	**Cumulative**
Lignite	5.63	17.88	8.88	32.39
10%OP + 90%L	23.62	7.81	5.25	36.68
20%OP + 80%L	27.66	8.91	5.25	36.68
30%OP + 70%L	30.50	10.60	2.80	43.91
40%OP + 60%L	34.11	13.01	1.93	49.05
50%OP + 50%L	40.65	15.81	0.41	56.87
Olive Pomace	69.22	12.07	1.83	83.12

Another point to be noted is that, even at the limited addition rates, lignite has a significant effect on the combustion profile: With the addition of olive pomace, the 1st region becomes the most efficient combustion region. In addition, the activation energy of the region increases significantly with the increase in the ratio of olive pomace in the mixture. This indicates an increase in the ratio of the olive pomace and the increase the contribution of the region to cumulative activation energy. The activation energy of the 2nd combustion region is also increasing steadily with the increase in the ratio of olive pomace. The effectiveness of the 3rd region considerably reduces due to the increase in the rate of olive pomace (Table 10).

In the light of all these data, it has been seen that, due to the increase in the additive ratio, the olive pomace significantly increased the combustion profile of lignite and caused significant differences when compared with the burning properties of the lignite. However, the presence of lignite in the mixture significantly improves the low combustion efficiency, which is probably the most critical issue in the use of the olive pomace. Therefore, it was seen that the results obtained with these two fuels together are not only important for lignite but also have critical importance and advantage for olive pomace.

6.5. Investigation of SO_2 Emissions of Lignite, Olive Pomace and Olive Pomace-Lignite Blends

One of the important objectives of the thesis is to reduce/rehabilitate the SO_2 emissions due to combustion, which is an important problem in the use of domestic lignite in Turkey. In this context, by using an Emission Gas Analysis (EGA) unit consisting of integrated Thermogravimetry (TG) – FTIR system as specified in the material and method section, olive pomace-lignite blends containing different amount of olive pomace and lignite samples were burned between 30-900°C and provided emission analysis. After analyzing the results obtained the analysis, SO_2 emissions were compared to the SO_2 emission profiles at the highest level, and the effects of the olive pomace addition and change in olive pomace ratio on SO_2 emissions were determined.

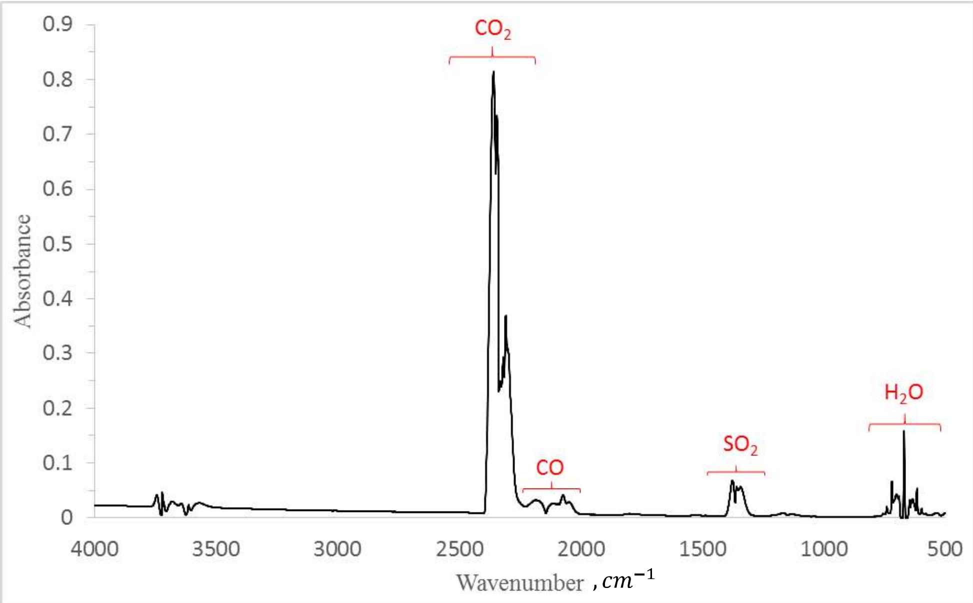


Figure 37. Emission profile of rom lignite sample at 300 °C

Typical gas emission profiles resulted by the combustion lignite and olive pomace samples during the combustion are shown in Figures 37 and 38. In the system, there are vast amount of libraries of infrared spectra available, allowing to compare unknown materials to ensure accurate identification. As seen in Figure 37, a significant amount of CO_2 was observed during the combustion of the lignite sample. The peaks, which is also called absorbance bands and/or serial peaks, corresponding to the CO_2 emission were seen in the range of about 2250-2500 cm^{-1}. In addition, a significant amount of water vapor, SO_2 emission and CO release also constituted other characteristic regions in FTIR spectrum: SO_2 emission was in the 1300-1410 cm^{-1} range and consisted of two separate bands. CO emission was seen in a relatively low and wide wavelength range (2000-2250 cm^{-1}) compared to CO_2 emission as expected. The characteristic absorbance bands-peak region showing the formation of water vapor was observed in the 600-750 cm^{-1} range (Figure 37).

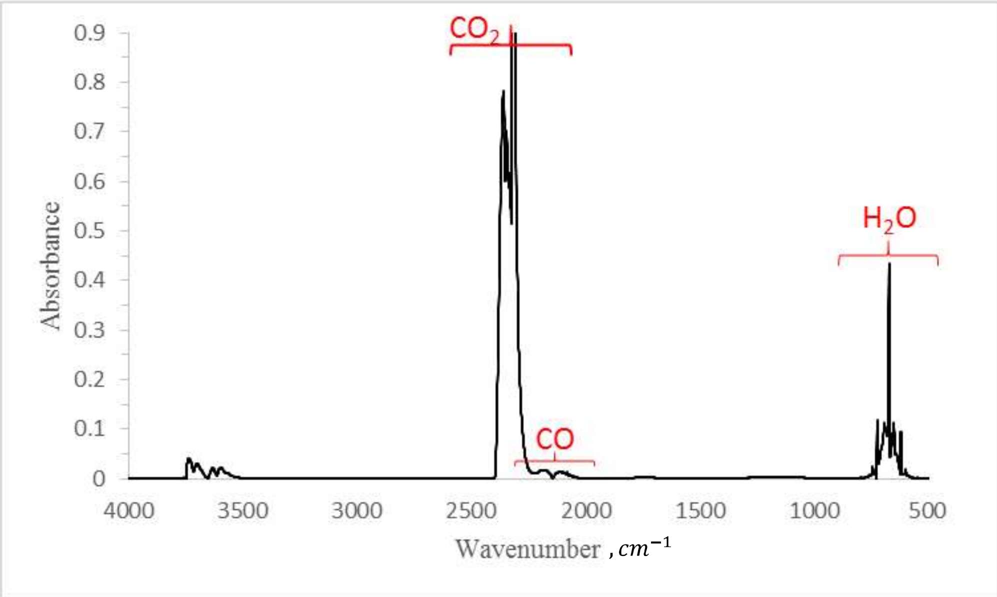


Figure 38. Emission profile of olive pomace sample at 300 °C

Typical gas analysis resulting of emissions from the combustion of the olive pomace at 300°C, that is emission profile, is shown in Figure 38. As a result of the burning of the olive pomace, the area of severe CO_2 emission in the range of 2250-2500 cm^{-1} and water vapor exhaust in the 600-750 cm^{-1} range were observed. The CO release in the 2000-2250 cm^{-1} range was lower than the lignite sample. When compared to the lignite sample, the most important difference in the typical emission profile of the olive pomace is that there was no absorbance band range indicating the SO_2 emission. In the proximate analysis of the olive pomace, the presence of Sulfur was not observed and the emission profile confirmed this situation.

In the light of the emission profiles obtained for the lignite and olive pomace samples, in order to examine the effect of the olive pomace addition on SO_2 emissions, the 1300-1410 cm^{-1} range was focused on which it is considered as the characteristic of the SO_2 emission part in the emission profiles of the different ratios of olive pomace. Considering the combustion behavior and thermal analysis results of the fuels examined in the study; representing the regions where the combustion reaction occurred in a severe and significant manner and also at the same time, considering temperatures that reach the highest level of SO_2 emissions in these regions, it was comparatively evaluated SO_2 emissions arises at 300°C, 375°C and 450°C. In this regard, it is shown that during combustion, the highest SO_2 emissions levels for mixtures that contain at different addition rate of olive pomace at 300°C in Figure 39, 375°C in Figure 40, and 450°C in Figure 41 comparatively and SO_2 emissions that arise as a result of the combustion of lignite alone and olive pomace alone.

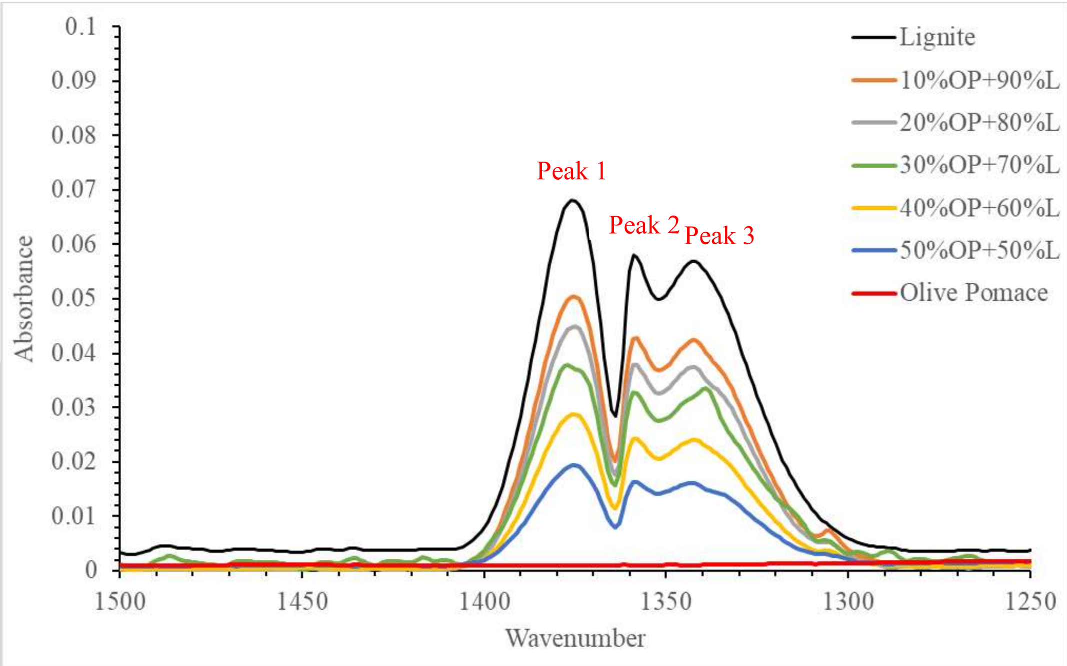


Figure 39. Comparative evaluation of SO_2 emissions at 300 °C

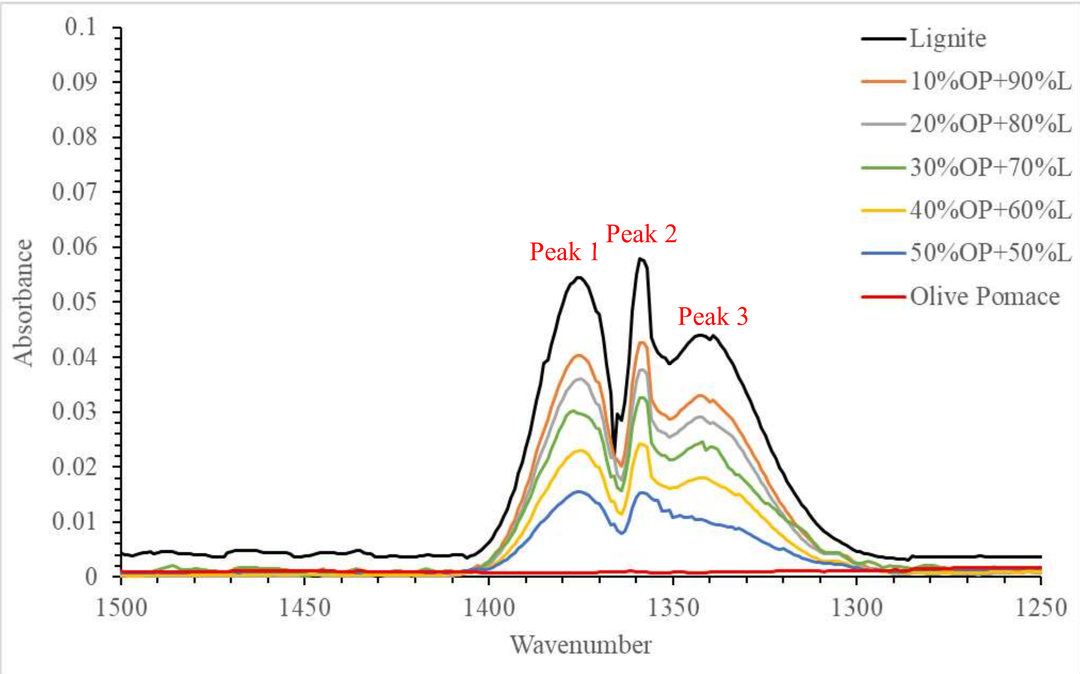


Figure 40. Comparative evaluation of SO_2 emissions at 375 °C

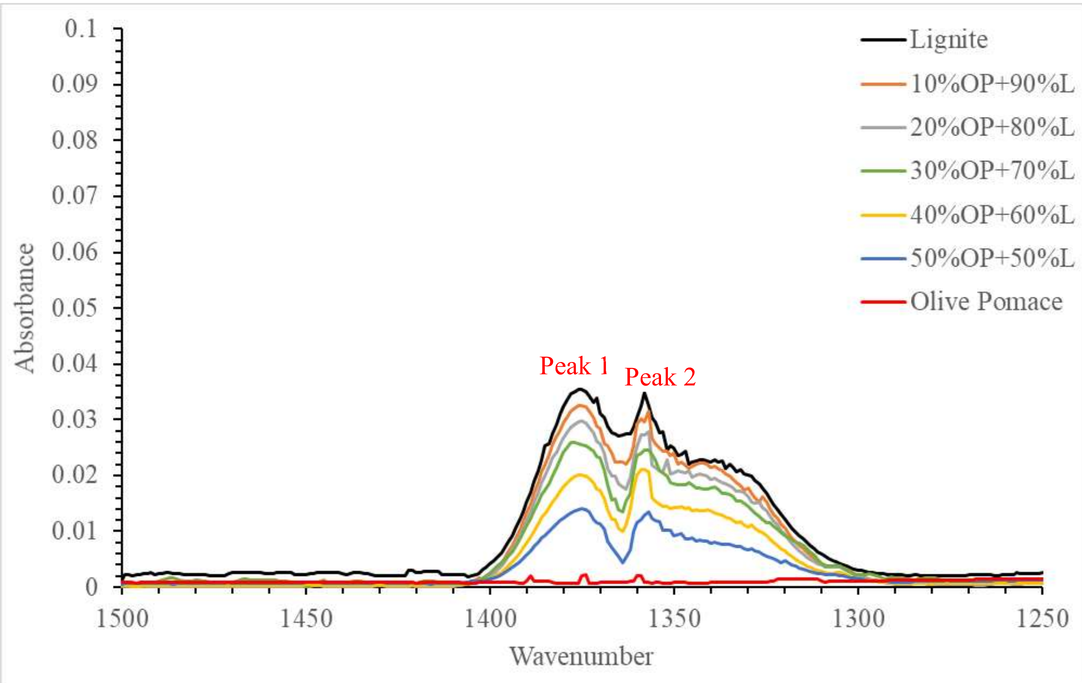


Figure 41. Comparative evaluation of SO_2 emissions at 450 °C

As it can be seen from the SO_2 emission profiles in Figure 39, 40, and 41, the SO_2 emission levels of the lignite, olive pomace, and olive pomace-lignite blends are different from each other. In addition, the positive effect of the olive pomace addition to reduce the SO_2 emissions is clearly seen at all temperature ranges discussed. At the temperatures considered, the highest levels of emissions were seen at 300°C, while the emissions seen at 375°C are close to the emissions seen at 300°C and the net SO_2 emission profiles were recorded at 450°C and also lower levels were seen. This is compatible with the DTG results obtained for the thermal behavior of fuels and mixtures: Relatively high SO_2 emissions occurring at 300°C and 375°C belong to the 1st and 2nd reaction regions, in which the combustion occurs severely, and therefore rate of weight loss is very high. In the 3rd reaction region, SO_2 emission levels were relatively low because of the fact that the reaction intensity is lower than the 1st and 2nd regions.

Three significant peaks were observed in the profile of SO_2 emission of R.O.M lignite at 300°C. The intensity of 3rd peak of R.O.M lignite decreased at 375°C. At 450°C, Peak 3 was completely lost and only two apparent peaks (Peak 1 and Peak 2) were observed. The SO_2 emission profiles and absorbance bands (lignite-olive pomace mixtures and olive pomace) recorded for the R.O.M lignite at three temperatures correspond to the highest absorption values. In the olive pomace sample, no apparent absorbance peak or region of SO_2 emissions were observed at all combustion temperatures. After olive pomace addition, it was seen that all SO_2 emission peaks seen in the R.O.M lignite decreased to the lower levels. In addition, SO_2 emission profiles in the 1300-1390 cm^{-1} were seen to have the lower levels (Figure 39-41): increasing the addition rate of olive pomace from 10% to 50%, SO_2 emission peak intensity decreased to lower levels at all temperatures. At 300 °C, the highest absorbance value (Peak 1) observed about in 1380 cm^{-1} was approximately 0.07 in R.O.M lignite, this value was reduced to about 0.05 with 10% olive pomace addition and when olive pomace addition reaches to 50%, it was below 0.02 (Figure 39). This situation was the same for Peak 2 and Peak 3 corresponding to SO_2 emission at 300°C.

At 50% olive pomace addition, Peak 2 and Peak 3 of R.O.M lignite almost lost their apparent forms. SO_2 emissions at 375°C were also same situation (Figure 40). The only difference is that Peak 2 achieved a slightly lower absorption value for the R.O.M lignite and olive pomace-lignite blends. In addition to this, absorbance bands of Peak 1, Peak 2, and Peak 3 were significantly reduced as the addition of olive pomace is increased from 10% to 50% in the mixtures. In other words, SO_2 emissions compared to the R.O.M lignite were reduced to the lower levels with the olive pomace addition (Figure 40). This was also the same for the rate of olive pomace addition to the mixtures in terms of SO_2 emission profiles at 450°C: SO_2 emissions were recorded as lower values with increasing amount of olive pomace in the mixtures compared to the R.O.M lignite. SO_2 emissions determined in Peak 1 and Peak 2 were reduced to the lower absorption values (Figure 41). Therefore, in all of the SO_2 emissions recorded at 300°C, 375°C, and 450°C, the positive effects of olive pomace addition on reducing SO_2 emissions was clearly observed and as proportions of olive pomace in blends increased, this positive effects also appeared at a higher level (Figure 39-41).

6.6. Evaluation of Strength Properties of Lignite Briquettes

6.6.1. Determination the Effect of Lignite Particle Size on the Strength Properties of Lignite Briquettes

In the determination of the strength properties of the fuel briquettes, as specified in the materials and method chapter, the tendency of lignite samples to briquette was determined. The result obtained at this stage were used as the reference in terms of the strength properties of the briquettes to be obtained with the addition of olive pomace. The diameter and length of the briquettes obtained at all stages of the study is equal to 5 cm.

In this context, firstly, the effect of particle size on briquette strength was determined. When 10% molasses as a binder and 9% water addition were constant, the briquettes were obtained with lignite samples that had 3, 6, and 9 mm P_{100} particle size under 3 tons briquetting pressure (≅ 15 MPa). Compressive strength, abrasion resistance, and impact resistance of the briquettes were determined by using procedures in TS12055 standard. Table 11 shows the strength properties of briquettes according to the particle size.

Table 11. Change in strength properties of lignite briquettes with respect to lignite particle size

	Lignite Particle Size (P_{100})		
	- 3 mm	**-6 mm**	**-9 mm**
Compressive Strength, kg/cm^2	138	125	108
Abrasion Resistance, %	52	74	72
Impact Resistance, %	70	84	77
Water Resistance, %	0*	0*	0*

*Briquettes cannot maintain their integrity in water for 1 hour.

As seen in Table 11, the highest compressive strength (138 kg/cm^2) was obtained using -3 mm particle size. This compressive strength value is higher than the required strength value for both Type I (130 kg/cm^2) and Type II (100 kg/cm^2) type briquettes in TS12055 standard. When the lignite particle size was increased, compressive strength of briquettes was negatively affected. As the particle size was increased to -6 mm and then -9 mm, the compressive strength decreased to 108 kg/cm^2. In terms of the compressive strength, the best result was obtained with –3 mm particle size, and the lowest strength results were obtained in terms of abrasion and impact resistance. Abrasion resistance of this particle size is 52% and impact resistance is 70% and these two values are below the lower limit values in TS12055 for Type I and Type II briquettes. When the lignite particle size was increased to -6 mm, abrasion resistance increased up to 74%, and briquettes obtained using -9 mm particle size had similar abrasion resistance. Lignite briquettes could not show water resistance required for both Type I and Type II type briquettes in TS12055 standard: lignite briquettes could not maintain their integrity in water no matter what particle size. They were dispersed in water without completing the waiting period of 1 hour as required in standard.

Therefore, for all particle sizes of briquettes, water resistance is not the matter. As stated in the beginning of the thesis, this situation and problem is related to many lignite types in Turkey. Therefore, briquettes are marketed in closed packages as stated in the related standard. When briquette strength is taken into consideration for lignite particle size, it was seen that the best results was obtained with -6 mm particle size. Despite the high compressive strength of briquettes obtained in -3mm particle size, abrasion and impact resistance of these briquettes were very low. -3 mm lignite particles have a higher surface area than larger particle sizes. This also means a wider area to be adhered and gathered by using binder. In this case, despite the high compressive strength, briquettes obtained with -3 mm particle size and 10% molasses were considered to be insufficient. In the case of -9 mm particle size, it was seen that the strength properties were very weak in strength properties especially compressive strength with respect to -6 mm particle size. When -9 mm size particles are used in briquetting, it was thought that there is more space between the particles, even under load, than -6 mm and -3 mm particle size. Even if the amount of binder is sufficient, it was also thought that these spaces cause weakness in terms of approaching particles one another and holding particles together. As a result of this situation, it was considered that briquettes obtained - 9 mm size particles were lower results especially in termsof compressive strength than briquettes obtained -3 mm and -6 mm size lignite particles.

The effect of particles size on the strength properties of briquettes was obtained with the best results using -6 mm lignite particle size in terms of abrasion and impact resistance (Table 11). The result obtained in terms of compressive strength was also improved. Therefore, the second stage that investigated the effect of water addition to briquette strength was continued with -6 mm lignite particle size.

6.6.2. Determination of the Effect of Water Addition on the Strength Properties of Lignite Briquettes

In the second stage, -6 mm lignite particle size and 10% molasses addition as a binder were kept constant and briquettes were obtained with addition of water at 3%, 6%, 9%, 12% and 15% by weight under 3 tons briquetting load (≅15 MPa pressure). The strength properties of the briquettes were given in Table 12 according to the water addition. The strength results obtained in the previous step for briquettes containing 9% of water by weight were also considered at this stage. As seen in Table 12, briquettes with the highest compressive strength were obtained by adding 6% of water amount. Compressive strength decreases when the amount of water is increased to over 6%, especially for briquettes containing 12% and 15% of water content showed significant decreases. The compressive strength of briquettes containing 6% of water addition was obtained as 132 kg/cm^2 and the compressive strength of briquettes containing 15% water addition was obtained as 102 kg/cm^2 value. In addition, the compressive strength of briquettes obtained with addition of 6% water provides the desired value for Type I briquettes in TS12055 standard.

Table 12. Change in strength properties of lignite briquettes with respect to addition of water amount

	Water Addition				
	3%	**6%**	**9%**	**12%**	**15%**
Compressive Strength, kg/cm^2	122	132	125	109	102
Abrasion Resistance, %	72	78	74	71	67
Impact Resistance, %	81	87	84	74	61
Water Resistance, %	0*	0*	0*	0*	0*

* Briquettes cannot maintain their integrity in water for 1 hour.

The best strength results in terms of abrasion resistance (78%) were obtained with briquettes obtained by adding 6% of water. This value meets the required abrasion resistance value (75%) for Type I briquettes in TS12055. When water addition ratio was increased to 9%, the abrasion resistance decreased slightly (74%), and with increasing amount of water addition rate was increased further, decrease in the abrasion resistance became apparent. For briquettes containing 15% of water amount, it decreased to 67% (Table 12). Lignite briquettes could not maintain their integrity in water no matter what rate of was added. In addition to this, they were dispersed in water without completing the waiting period in 1 hour required in standard (Table 12).

Briquettes containing 6% of water addition gave the best strength results in terms of impact resistance and the value was obtained aqs 87% (Table 12). The increase in the water addition adversely affected the impact resistance of briquettes similar to the compressive strength and abrasion resistance. Impact resistances were obtained as 84%, 74%, 61% with 9%, 12% and 15% of water addition, respectively. Impact resistance of briquettes obtained with 3% of water addition was lower than the impact resistance of briquettes with 6% of water addition. In the TS12055 standard, required impact resistance for Type 2 briquettes is 80% and for Type I briquettes is 90%. Therefore, the highest impact resistance of briquettes obtained using 6% of water addition provided required impact resistance for Type II briquettes and approached to Type I condition.

When the water addition and the strength of the briquettes were evaluated together, it is seen that briquettes with the highest strength properties are obtained with 6% of water addition by weight in terms of all strength parameters. In other words, increasing water amount from 3% to 6% improves the strength properties of briquettes, but water addition rates higher than 6% adversely affect the strength properties of briquettes. This situation was observed for briquettes with 12% and 15% water amount. In the light of these data, lignite samples obtained with -6 mm lignite particle size and 6% water addition were used in the third stage in which strength of briquettes and effects of briquetting pressure were investigated.

6.6.3. Determination of the Effect of Briquetting Pressure on the Strength Properties of Lignite Briquettes

In the third stage, -6 mm lignite particle size, 10% molasses addition as a binder and %6 of water addition were kept constant and lignite-olive pomace-water mixtures were briquetted under 1, 2, 3, 4, and 5 tons briquetting pressures. According to the applied briquetting pressure, the strength properties of briquettes are given in Table 13. In the previous stage, the strength results of briquettes obtained with 6% of water addition by weight and under 3 tons briquetting pressure were also taken into consideration at this stage.

The highest compressive strength of briquettes (147 kg/cm^2) was obtained under 5 tons briquetting pressure. The compressive strengths of briquettes under 3 and 4 tons load were higher than 130 kg/cm^2 and provided the conditions for Type I briquettes in TS12055 standard (Table 13). Briquettes obtained under 1 and 2 tons load could not provide good results in terms of compressive strength. Especially, briquettes obtained under 1 ton load had very low compressive strength (79 kg/cm^2). With respect to the abrasion resistance, briquettes obtained under 1 and 2 tons load remained low, but at 3 tons and higher briquetting pressure required abrasion resistance for Type I briquettes was achieved as provided in TS12055. When briquetting pressure was increased from 3 tons to 4 tons, abrasion resistance had much better results (87%). As briquetting load was increased to 5 tons, there was no additional improvement in the abrasion resistance (Table 13). When the briquetting pressure was increased, it was seen that abrasion resistance also increased. However, impact resistance obtained under 1 and 2 tons load could not reach the required level and it could not meet even the required strength properties of Type II briquettes. When briquetting pressure was increased to 3 tons, impact resistance value for Type I briquettes in standard approached the value of 90%. Briquettes obtained under 4 and 5 tons load had higher values than the required. Lignite briquettes could not achieve water resistance at this stage. In all tests done for all briquetting pressure levels, briquettes left in water were dispersed in water and lost their integrity before 1 hour waiting period was completed (Table 13).

Table 13. Change in strength properties of lignite briquettes with respect to briquetting load(pressure)

	Briquetting Load (Pressure)				
	1 ton (≅5 MPa)	**2 ton (≅10 MPa)**	**3 ton (≅15 MPa)**	**4 ton (≅20 MPa)**	**5 ton (≅25 MPa)**
Compressive Strength, kg/cm^2	79	108	132	145	147
Abrasion Resistance, %	63	71	78	87	87
Impact Resistance, %	61	76	87	95	93
Water Resistance, %	0*	0*	0*	0*	0*

* Briquettes cannot maintain their integrity in water for 1 hour.

Taking the effects of strength properties into the briquetting load, it was clear that applying of 1 and 2 tons load were insufficient to obtain briquettes with desired strength properties. The strength properties of the briquettes with 3, 4, and 5 tons of load were improved and compressive strength and abrasion resistance for Type I briquettes were nearly higher than the required values as described in the related standard. The required impact resistance for Type I briquettes could be obtained briquettes using with 4 and 5 tons of briquetting load. In these loads, compressive strength and abrasion resistance of briquettes were also improved. When the results were evaluated comparatively, it was seen that 4 tons load is the ideal briquetting load that get the briquettes with desired strength properties. Therefore, briquettes obtained in the next stages of study were briquetted under 4 tons load. In this context, when the load was increased from 4 tons to 5 tons, no significant improvement was observed in the strength properties of the briquettes.

6.7. Determination of Strength Properties of Binderless Hybrid Fuels (Olive Pomace-Lignite) Briquettes

6.7.1. Determination of the Effect of Olive Pomace Moisture Content on the Strength Properties of Binderless Hybrid Briquettes

Following the determination of the strength properties of lignite briquettes, it was proceeded to obtain olive pomace-lignite mixture without binder and determine the strength properties of the binderless hybrid briquettes. At this stage, the diameter and the length of the briquettes were also 5 cm.

In this context, firstly, the effect of the olive pomace moisture content on the strength properties of binderless hybrid briquettes was determined. At this stage, briquettes of olive pomace-blends mixtures containing 30% olive pomace and 70% lignite by weight were obtained under 4 tons load (≅20 MPa pressure) containing 9 mm olive pomace size(P_{100}) and 6 mm lignite size samples. Moisture content of olive pomace was changed between 5-25% with 5% increments. Then, compressive strength, abrasion resistance and impact resistance of binderless hybrid briquettes were determined by using test procedures detailed in the material-method part. Table 14 shows the strength properties of binderless hybrid briquettes according to their moisture content.

Table 14. Change in strength properties of binderless hybrid briquettes with respect to moisture content

	Moisture Content (%)				
	5	**10**	**15**	**20**	**25**
Compressive Strength, kg/cm^2	67	75	73	66	58
Abrasion Resistance, %	53	57	56	50	43
Impact Resistance, %	41	47	44	38	30
Water Resistance, %	0*	0*	0*	0*	0*

* Briquettes cannot maintain their integrity in water for 1 hour.

When the moisture content is increased from 5% to 10%, it was observed that compressive strength of briquettes increased. However, when it is increased from 10% to 15%, it was observed that compressive strength values decreased a little. In case that moisture content is more than 15%, compressive strengths of briquettes were adversely affected and compressive strength value decreased to 58 kg/cm^2 when moisture content is 25% (Table 14). In terms of abrasion and impact resistance, there is a similar situation to the compressive strength; when the moisture content is increased from 5% to 10%, abrasion and impact resistance of the briquettes increases. When the moisture content is increased from 10% to 15%, abrasion resistance remained almost at the same level but impact resistance decreased a little. When the moisture content is increased more than 15%, both abrasion and impact resistance of briquettes decreased significantly. At this stage, the lowest abrasion resistance value (43%) and the lowest impact resistance value (30%) for binderless hybrid briquettes were obtained with 25% moisture content (Table 14). Hybrid briquettes without binder could not provide the desired strength properties in TS12055 standard at any olive pomace moisture content. Hybrid briquettes were dispersed in water without completing the waiting period in 1 hour required in standard and they could not maintain their integrity in water no matter what the olive pomace moisture content is.

As seen in Table 14, the highest compressive strength is 75 kg/cm^2, the highest abrasion resistance is 57% and the highest impact resistance is 47% for binderless olive pomace-lignite briquettes. These values were obtained with 10% moisture content of olive pomace. In other words, critical level of olive pomace moisture content is 10 % for binderless hybrid briquettes. Strength properties were improved until 10% moisture content but when moisture content is increased to 15%, strength properties decreased a little. Moisture content above 15% adversely affected the strength properties of briquettes. Especially, the strength values obtained at 25% moisture level are very low.

Although 10% moisture content of olive pomace provides the highest strength properties, obtained strength values are lower than the limit values required for both Type 1 and Type 2 briquettes in TS12055 standard. As a result, strength properties of binderless hybrid briquettes were continued to the next stages with 10% olive pomace moisture content.

6.7.2. Determination of the Effect of Olive Pomace Particle Size on the Strength Properties of Binderless Hybrid Briquettes

In the second stage, the effect of olive pomace particle size on the strength properties of binderless hybrid briquettes were determined. Mixtures containing 30% olive pomace and 70% lignite by weight were briquetted under 4 tons (≅20 MPa pressure) briquetting load. In the mixtures, olive pomace particle size (P_{100}) was changed from 3-15 mm while lignite particle size (P_{100}) was used as 6 mm. Moisture content of the olive pomace was kept constant at 10%, which was the ideal value determined in the previous stage. Then, compressive strength, abrasion resistance, and impact resistance of binderless hybrid briquettes were determined by using test procedures detailed in the material-method part. Table 15 shows the strength properties of binderless hybrid briquettes according to different olive pomace particle sizes.

Table 15. Change in strength properties of binderless hybrid briquettes with respect to particle size of olive pomace

	Olive Pomace Particle Size, P_{100} (mm)				
	3	**6**	**9**	**12**	**15**
Compressive Strength, kg/cm²	83	77	75	66	55
Abrasion Resistance, %	64	59	57	52	48
Impact Resistance, %	59	51	47	40	30
Water Resistance, %	0*	0*	0*	0*	0*

* Briquettes cannot maintain their integrity in water for 1 hour.

When evaluating the strength properties of briquettes obtained with respect to olive pomace particle size, it was seen that decreasing olive pomace particle size was improved the strength characteristics of briquettes generally. Parallel to this situation, the lowest compressive strength (55 kg/cm^2), the lowest abrasion resistance (48%) and the lowest impact resistance (30%) values were obtained with -15 mm olive pomace particle size for binderless hybrid briquettes at this stage. As the olive pomace size decreases, strengths of briquettes increase significantly, and all strengths of briquettes were improved. Decreasing the particle size of olive pomace from -15 mm to -9 mm provided an increase of the compressive strength value from 55 kg/cm^2 to 75 kg/cm^2, the abrasion resistance from 48% to 57%, and the impact resistance from 30% to 47%. In addition, decreasing the particle size from -9 mm to -3 mm resulted in better strength values where compressive strength of 83 kg/cm^2, abrasion resistance of 64% and impact resistance of 59% was reached (Table 15). Therefore, the highest strength values for binderless hybrid briquettes were obtained with 3 mm (P_{100}) particle size of olive pomace. This situation can be interpreted as olive pomace particle size decreases; not only more homogeneous olive pomace-lignite mixtures can be obtained but also depending on the increasing surface area, more effective contact, and interaction between the lignite and olive pomace particles. In addition, as the particle size increases, there is more space between the particles even under load. These spaces can lead to weakness in terms of approaching the particles and keeping them together. When olive pomace particle sizes, which are expected to show a binding property, decreases, it is thought that the space between particles can be better filled and that the particles can hold on to each other more effectively. The water resistance properties of the binderless hybrid briquettes could not be improved by changing particle size of olive pomace. In all olive pomace particle sizes, binderless hybrid briquettes left in waterdispersed in water and lost their integrity before 1 hour waiting period was completed. They could not maintain their integrity in water no matter what olive pomace particle size is (Table 15). The strength values obtained using -3 mm olive pomace particle size exceeded the strength values obtained in the previous stage (Table 14 and 15). Despite this situation, strength values obtained at this stage still remain below the limit values required for Type I and Type II briquettes in the TS12055 standard.

6.7.3. Determination of the Effect of Olive Pomace Addition Rate on the Strength Properties of Binderless Hybrid Briquettes

In this stage, olive pomace-lignite mixtures were briquetted without binder and the effect of addition rate of olive pomace in the mixtures on the strength properties of the hybrid briquettes was determined. In the light of the ideal conditions obtained in the previous stages, binderless hybrid briquettes were briquetted with 3 mm (P_{100}) olive pomace size and 6 mm (P_{100}) lignite particles under 4 tons load (≅20 MPa pressure). In the mixtures, the ideal moisture content rate of olive pomace was kept constant as 10%. The added amount of olive pomace in the mixture was changed between 10-50% by weight in 10% increments. Hybrid briquettes containing different ratio of olive pomace by weight were subjected to the compressive strength, abrasion, and impact resistance tests according to the procedures detailed in the material-method chapter. The strength properties obtained at this stage are given collectively in Table 16.

Table 16. Change in strength properties of binderless hybrid briquettes with respect to the addition rate of olive pomace

	Ratio of Olive Pomace, (by wt,%)				
	10	**20**	**30**	**40**	**50**
Compressive Strength, kg/cm²	72	78	83	75	62
Abrasion Resistance, %	54	60	64	57	50
Impact Resistance, %	48	54	59	51	38
Water Resistance, %	0*	0*	0*	0*	0*

* Briquettes cannot maintain their integrity in water for 1 hour.

The strength of the briquettes improves when the amount of olive pomace is increased from 10% to 20% then to 30% by weight. The compressive strength increased from 72 kg/cm^2 to 83 kg/cm^2, abrasion resistance increased from 54% to 64%, and impact resistance increased from 48% to 59% (Table 16). Strength properties of hybrid briquettes containing 40% and 50% olive pomace by weight was lower than the briquettes containing 30% by weight. In other words, the addition of more than 30% of olive pomace addition to the mixture adversely affects the strengths of hybrid briquettes. As a result of this situation, the weakest briquettes were obtained with 50% amount of olive pomace in terms of compressive strength, abrasion resistance, and impact resistance. Olive pomace-lignite mixtures containing 30% of olive pomace amount provided the highest strength in terms of three strengths. Water resistance properties of the binderless hybrid briquettes are not different from previous stages. They could not be improved by changing addition rate of olive pomace. In all olive pomace addition rate, binderless hybrid briquettes left in water dispersed in water and lost their integrity before 1 hour waiting period was completed. They could not maintain their integrity in water no matter what olive pomace amount is (Table 16).

Strength values for the hybrid briquettes using ideal conditions determined up to this stage and addition of 30% olive pomace have the highest strength values obtained for the binderless hybrid briquettes at this stage of the study. But yet, these values could not meet the requirements for Type I and Type II briquettes. However, the limit abrasion value (65%) required for Type II briquettes was approximately achieved very close and significant improvements have been achieved in terms of compressive strength.

6.7.4. Evaluation of Briquetting Parameters and Studies for Improvement of Strength Properties of Hybrid Briquettes

In the briquetting of olive pomace-lignite mixtures, moisture content, particle size and amount of olive pomace were considered as the main parameters given in the beginning of the study. As a result of the studies, it has been seen that olive pomace has binding property but this property is not strong as molasses, which is a commonly used binder in coal briquetting. In this regard, in the briquetting of olive pomace-lignite mixtures without binder, when ideal briquetting conditions were determined step by step and under parameters mentioned above, compressive strength, abrasion and impact resistance values of briquettes were improved. 10% moisture content, -3 mm olive pomace particle size and 30% ratio of olive pomace that were determined as the ideal conditions were obtained at the highest strength values (Table 16). Compressive strength and impact resistance obtained do not meet the requirements for Type 1 and Type 2 briquettes in the TS12055 standard and abrasion resistance provides the necessary condition for Type 2 briquettes.

In the light of these finding, additional changes were made to the briquetting parameters and the strength properties of binderless hybrid briquettes were tried to be improved. In this context, ratio of olive pomace in mixtures was discussed in more detail since olive pomace has binding property, leastwise. When the ratio of olive pomace was changing 30% and 40% in 2.5% increments, hybrid briquettes were subjected to the strength tests. In addition, the briquetting pressure was also considered and the load level was raised above 4 tons (≅20 MPa pressure). In this context, hybrid briquettes were obtained by increasing briquetting pressure to 4.5 tons (≅22.5 MPa pressure) and 5 tons (≅25 MPa pressure) by using the ideal ratio of olive pomace and after that briquettes were subjected to the strength tests. Strength properties obtained by varying olive pomace amount in the range of 30-40% are shown in Table 17 and strength properties obtained by increasing the briquetting load level are shown in Table 18.

Table 17. Change in strength properties of binderless hybrid briquettes with respect to the ratio of olive pomace between 30-40% by wt

	Ratio of Olive Pomace , (by wt,%)				
	30	**32.5**	**35**	**37.5**	**40**
Compressive Strength, kg/cm^2	83	86	88	85	75
Abrasion Resistance, %	64	66	66	63	57
Impact Resistance, %	59	62	63	60	51
Water Resistance, %	0*	0*	0*	0*	0*

* Briquettes cannot maintain their integrity in water for 1 hour.

Table 18. Change in strength properties of binderless hybrid briquettes with respect to briquetting load (pressure)

	Briquetting Load (Pressure)		
	4 ton (20 MPa)	**4.5 ton (22.5 MPa)**	**5 ton (25 MPa)**
Compressive Strength, kg/cm^2	88	93	92
Abrasion Resistance, %	66	69	70
Impact Resistance, %	63	69	68
Water Resistance, %	0*	0*	0*

* Briquettes cannot maintain their integrity in water for 1 hour.

It can be seen that changing the addition of olive pomace with 30-40 % (by wt) resulted in changes in the strength properties of the briquettes in Table 17. When the ratio of olive pomace was increased from 30% to 35% (with 2.5% increments), the compressive strength and impact resistance of briquettes improved more, and abrasion resistance of briquettes improved less. 35% of olive pomace is a critical level and strength properties of briquettes get worse above this value (37.5% and 40%). In this context, 37.5% amount of olive pomace is an important point. Moreover, when ratio of olive pomace is increased from 37.5% to 40%, there was a significance decrease in the values of compressive strength, abrasion resistance and impact resistance. Therefore, the ideal value for the addition of olive pomace in binderless hybrid briquettes was 35% by weight (Table 17), and mixtures of olive pomace and lignite were used with 35% olive pomace amount by weight in the next step in which the effect of the briquetting load on the strength properties of the hybrid briquettes was examined. As shown in Table 18, increasing the briquetting load from 4 tons to 4.5. tons gave positive results in terms of especially compressive strength and impact resistance and improved the abrasion resistance at limited value. Increasing the briquetting load from 4.5 tons to 5 tons could not significantly change the strength properties of the briquettes. Strength values obtained applying the 4.5 tons and 5 tons briquetting load in terms of compressive strength, abrasion resistance and impact resistance were almost the same (Table 18).

Both changing the olive pomace addition in range of 30-40% and changing the briquetting load in the range of 4-5 tons could not lead to an improvement in the strength of the binderless hybrid briquettes. In all olive pomace addition rate and briquetting load, binderless hybrid briquettes left in water were dispersed in water and lost their integrity before 1 hour waiting period was completed. In other words, binderless hybrid briquettes could not maintain their integrity in water under these conditions (Table 17 and 18).

In the lights of results given in Table 17 and 18, the strength properties of binderless hybrid briquettes was improved a little as a result of the detailed analysis of olive pomace addition. Compressive strength of briquettes with 35% olive pomace addition increased to 93 kg/cm^2, abrasion resistance increased to 69 % and impact resistance increased to 69 % at 4.5 tons of briquetting load. According to TS12055, when the obtained strength values were evaluated in terms of conditions for Type I and Type II briquettes according to TS12055 standard, it was seen that the limit strength values for Type I could not be reached. However, the abrasion resistance value required for Type II briquettes can be exceeded required value (65%) and compressive strength is very close to required limit value (100 kg/cm^2). Impact resistance was the weakest strength in binderless hybrid briquettes. Impact resistance value (69%) obtained in ideal cases was lower than the required value (80%) for Type II briquettes.

6.8. Determination of Strength Properties of Hybrid Briquettes with Binder

Hybrid lignite-olive pomace briquettes were determined to show a certain degree of strength using without binder: when hybrid briquettes are briquetted without binder, they had low strength values than that of hybrid briquettes with binder. By the tests performed, briquetting conditions were determined and it was concluded that olive pomace has binding property to a certain extent. Therefore, hybrid briquettes provide the required abrasion resistance value for Type II briquettes and compressive strength values significantly approach to achieve the required value. However, strength values of binderless hybrid briquettes could not achieve the required value for Type I briquettes in TS12055 standard. In other words, it has been found that it may be necessary to use binders in order to attain the strength values of hybrid lignite-olive pomace briquettes for Type I briquettes.

Accordingly, at this stage, hybrid briquettes were obtained by the addition of binders to lignite-olive pomace mixtures within the ideal briquetting conditions determined in the previous stages of the study. In this context, only molasses was used as a binder and strength values of the hybrid briquettes containing molasses in varying proportions were determined. In the lights of obtained strength values, following the determination of the ideal amount of molasses, hybrid briquettes with molasses and lime as binders were obtained for second stage and also determined the addition of lime in terms of the strength values. As in the earlier stages of the study, the diameter and length of the briquettes obtained at this stage are equal to 5 cm.

6.8.1. Determination of the Effects of Addition of Molasses on Strength Properties of Hybrid Briquettes in case of Only Molasses as a Binder

At this stage, hybrid briquettes containing only molasses were obtained using ideal briquetting conditions that were used for briquettes with only lignite and binderless hybrid briquettes. Mixture containing olive pomace amount of 35% by weight (P_{100} = 3 mm) and lignite amount of 65% by weight with 105 of moisture content of blends were briquetted under briquetting load of 4.5 tons (≅ 22.5 MPa). The amount of molasses used by obtaining of hybrid briquettes was changed by 5 – 15% by weight in 5% increments. Hybrid briquettes obtained in this way were subjected to strength tests that are compressive strength, abrasion resistance, impact resistance, and water resistance in the procedures given in the material-method section. Table 19 shows the strength properties of hybrid olive pomace – lignite briquettes depending on the amount of molasses.

Table 19. Change in strength properties of hybrid briquettes with respect to amount of molasses addition

	Addition Amount of Molasses (by wt, %)		
	5	**10**	**15**
Compressive Strength, kg/cm^2	132	150	155
Abrasion Resistance, %	77	90	91
Impact Resistance, %	87	96	96
Water Resistance, %	0*	0*	0*

* Briquettes cannot maintain their integrity in water for 1 hour.

In the light of the results in Table 19, when amount of molasses was increased from 5% to 10% and to 15%, respectively, compressive strength of the briquettes increased and it reached the highest value (155 kg/cm^2) using 15% molasses addition rate. When the addition rate of molasses was increased from 5% to 10%, increase in the compressive strength, from 132 kg/cm^2 to150 kg/cm^2, is remarkable. In terms of abrasion and impact resistance, addition rate of molasses was increased from 5% to 10%, the positive differences occurred: when addition rate of molasses was increased from 5% to 10%, the abrasion resistance increased from 77% to 90% and the impact resistance increased from 87% to 96%. Moreover, when addition rate of molasses was increased from 10% to 15%, the abrasion and impact resistance of briquettes remained at the same levels (Table 19). Hybrid briquettes with molasses produced with all addition rates of molasses totally provided the required abrasion resistance (for Type I = 75% and for Type II = 65%) and compressive strength (for Type I = 130 kg/cm^2 and for Type II = 100 kg/cm^2) and in fact exceeded the desired strength levels both Type I and Type II briquettes at TS12055 standard. Required impact resistance (for Type I = 90% and for Type II = 80%) easily was provided by adding 10% and 15% of molasses amount (impact resistance value = 96%) and it could not be obtained by adding 5% molasses rate (impact resistance value = 87%) (Table 19). In all molasses addition rates, hybrid briquettes left in water were dispersed in water and lost their integrity before 1 hour waiting period was completed. In other words, hybrid briquettes with molasses whatever addition amount could not give any water resistance property (Table 19).

As shown in Table 19, the highest compressive strength, abrasion and impact resistance values (155 kg/cm^2, 91%, and 96%, respectively) were obtained with 15% molasses addition rate. Strength values obtained at 15% and 10% molasses addition rate are very close (especially for abrasion and impact resistance). In case of hybrid briquettes with binder addition, increasing addition rate of molasses from 10% to 15% did not lead to very significant differences in the strength properties. Required strength values (except water resistance) of hybrid briquettes with 10% molasses addition rate were provided easily for Type I briquettes in TS12055. At the same time, even the addition of 5% molasses significantly improved the strength characteristics of hybrid briquettes when compared to the binderless hybrid briquettes (Table 14-18): In case of binderless briquetting, strength properties could not meet the requirements under no circumstances for Type I briquettes and when only 5% molasses addition as a binder was added to the mixtures, strength properties were tolerable results for Type I briquettes: the compressive strength and abrasion resistance were met the required strength values and impact resistance value was very close to the required value (Table 19). This situation shows that due to the binding property of olive pomace, even limited, required strength properties of Type I hybrid briquettes can be met even with only 5% molasses addition. In other words, the presence of olive pomace has a positive effect by reducing the amount of binder that should be used.

In summary, in the context of molasses addition, ideal amount appears 10% addition rate for hybrid briquettes. At the same time, the addition of 5% molasses provides highly acceptable strength properties. In the study, the next stage that is related to the addition of lime is stated that will be at the ideal amount of molasses. However, due to the positive results obtained with the addition of molasses at both 5% and 10%, it was decided that the next stage of lime addition would be investigated in more detail with hybrid briquettes containing 5% and 10% molasses.

6.8.2. Determination of the Effects of Addition of Lime on Strength Properties of Hybrid Briquettes in case of Molasses and Lime as Binders

Similar to the previous step, in the investigation of binding effect of lime, ideal briquetting conditions that were the briquettes contained only lignite and the briquettes obtained without binder (35% by wt. of olive pomace with P_{100} = 3 mm + 65% by wt of lignite with P_{100} = 6 mm and briquetting load = 4.5 tons) were used. As indicated in the previous section, the addition of lime was done with molasses both 5% and 10% addition rate at this stage. In addition to the molasses, hybrid briquettes with binder were obtained using also 4% and 6% of lime addition. Briquettes obtained with both molasses and lime addition were subjected to the compressive strength, abrasion resistance, impact resistance, and water resistance tests within the procedures in the material-method chapter. Table 20 shows the strength properties of the hybrid olive pomace-lignite briquettes containing 5% of molasses addition depending on the amount of lime addition. Also, Table 21 shows the strength properties of the hybrid olive pomace-lignite containing 10% of molasses addition depending on the amount of lime addition.

Table 20. Change in strength properties of hybrid briquettes containing 5% molasses and varying amounts of lime according to the amounts of lime addition

	Amount of Lime * (by wt, %)		
	0	**4**	**6**
Compressive Strength, kg/cm^2	132	136	138
Abrasion Resistance, %	77	79	79
Impact Resistance, %	87	90	91
Water Resistance, %	0**	0**	0**

* Molasses addition rate was constant and it was 5% by wt.

** Briquettes cannot maintain their integrity in water for 1 hour.

Table 21. Change in strength properties of hybrid briquettes containing 10% molasses and varying amounts of lime according to the amounts of lime addition

	Amount of Lime * (by wt, %)		
	0	**4**	**6**
Compressive Strength, kg/cm^2	150	156	156
Abrasion Resistance, %	90	93	94
Impact Resistance, %	96	97	96
Water Resistance, %	0	0	0

* Molasses addition rate was constant and it was 10% by wt.

** Briquettes cannot maintain their integrity in water for 1 hour.

In the light of the results in Table 20, when the comparing strength properties of hybrid briquettes containing no lime and 4% of lime with 5% of molasses for both cases, strength properties of hybrid briquettes increased in terms of the compressive strength, abrasion resistance, and impact resistance but these increases were limited. When the lime addition was increased from 4% to 6%, the strength properties either increased a considerable amount or remained at same level. Hybrid briquettes containing 5% of molasses and varying amounts of lime were unable to withstand water as previous steps: In addition to molasses addition, briquettes with 4% and 6% of lime addition left in water were dispersed in water and lost their integrity before 1 hour waiting period was completed. In summary, in case of 5% of molasses addition, the use of lime as an additional binder increased the compressive strength slightly from 132 kg/cm^2 to 138 kg/cm^2 and did not cause any significance change in terms of the abrasion resistance. The water resistance of hybrid briquettes could not improve after the addition of lime. The most important benefit of the use of lime as an additional binder is that hybrid briquettes which have 5% of molasses addition after a limited increase in impact resistance have completely met the requirement of impact resistance for Type 1 briquettes (90%): the impact resistance increased to 90% after 4% of lime addition and to 91% after 6% of lime addition (Table 20).

When the results in Table 21 were examined, the effect of lime addition with 10% molasses added is similar to the results obtained with 5% molasses and lime addition: when comparing strength properties of hybrid briquettes containing no lime and 4% of lime, it is seen that strength properties of hybrid briquettes improved a little in terms of the compressive strength, slightly improved in terms of abrasion resistance, and could showed no change in terms of impact resistance. In case of 10% molasses addition, increasing the addition of lime from 4% to 6% did not lead to any significant change or improvement in terms of compressive strength, abrasion resistance, and impact resistance (Table 21). Addition of lime could not give any improvement in terms of water resistance. In addition to 10% of molasses addition, briquettes with 4% and 6% of lime addition left in water were dispersed in water and lost their integrity before 1 hour waiting period was completed.

In summary, the use of lime as a binder with molasses was far from providing the expected properties in terms of the strength properties of the hybrid briquettes. The lime addition could not improve the water resistance properties of the briquettes. Limited changes or improvements in compressive strength, abrasion, and impact resistance showed that the use of lime in combination with molasses has no critical role or contribution in obtaining hybrid briquettes: with the addition of 10% molasses only, the required strength conditions, except for water resistance, for Type I and Type II were provided. Even with the addition of 5% molasses, it was seen that the required strength conditions, except for water resistance, for Type I were achieved to a great extent. Therefore, it was found that the use of lime together with molasses as binders was not a necessary application in the production of hybrid lignite-olive pomace briquettes, since it could not produce an additional improvement in water resistance.

CHAPTER 7

CONCLUSION AND RECOMMENDATION

It is possible to examine the results in two categories. The first one is results of studies on fuel properties and combustion behavior of fuels and hybrid blends containing these fuels. The second one is results of studies aimed at the production of briquettes for the purpose of obtaining hybrid fuel form from the lignite-olive pomace mixtures.

In this context, the following results were obtained in the studies on the investigation of the fuel properties and combustion behavior of olive pomace and lignite and olive pomace-lignite mixtures:

- The findings of fuel properties and combustion behaviors of blends obtained in this section have been the first in the literature in terms of revealing the fuel properties and combustion behavior of olive pomace-lignite mixtures in detail.
- The addition of olive pomace to the lignite provides an important advantage in terms of controlling and reducing the SO_2 emissions.
- The use of lignite together with olive pomace in the hybrid fuel form can be much more favorable and appropriate rather than being used lignite alone as fuel. This is because it is possible to rehabilitate low tendency of the olive pomace to burn with the lignite addition.
- The proposed hybrid fuel is an innovative form of fuel that gives the positive characteristics of lignite and olive pomace prominence and significantly eliminates their negative properties.

The important results about various parameters that affect the briquetting process obtained in these studies are as follows:

- It was determined that lignite could be briquetted successfully using 10% of molasses by weight as a binder when examining the briquetting ability of hybrid blends.
- The results show that olive pomace has a binding effect in briquetting, but this effect cannot be as strong as the binding effect of agents commonly used in briquetting such as molasses.
- The presence of olive pomace has a positive effect as it can reduce the amount of binder needed to be used in briquetting.
- Any briquetting condition provides water resistance for both lignite briquettes and hybrid briquettes.

This study deals with the possibility of using fossil fuel and biomass resources together in a hybrid form in many ways. Some suggestions for some future researches and investigations are given below:

- In the form of fossil fuel-biomass hybrid fuel, instead of lignite, it will be useful to include alternative fossil fuels such as asphaltite and bituminous schist that are available in Turkey.
- There are biomass sources alternative to the olive pomace such as some organic agricultural residuals, paper industry residues, forest and wood industry waste in Turkey.
- Investigation of the combustion behavior of the hybrid fossil fuel-biomass briquettes in various reactors (eg for household heating), free combustion as well as controlled combustion and emissions resulting from free combustion (especially SO_2 emissions) will be the right decision.
- A specific study focusing only on solutions and methods to improve the water resistance properties of hybrid briquettes will be useful for taking into consideration of alternative fossil fuel and/or biomass.

For special uses as an alternative to briquetting, a similar study on the production of hybrid fossil fuel-biomass pellets should also be included in future studies.

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