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BRIQUETTING OF COAL – BIOMASS BLENDS

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ABBREVIATIONS

ASTM	:	American Society for Testing and Materials
DTG	:	Differential Thermogravimetry
ISO	:	International Organization for Standardization
TG	:	Thermogravimetry
TS	:	Turkish Standards
TSR	:	Thick Syrup Residuum

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BRIQUETTING OF COAL – BIOMASS BLENDS

SUMMARY

Most of lignites can easily be converted to dust. The lignite dusts are not suitable to be burned in stoves equipped with grates or central heating furnaces, since they are carried away from chimney without burning, and owing to some difficulties take place during transportation and storage of the coal dust. Thus, lignite reserves in Turkey are limitedly used as domestic fuels. However, increase in the use of Turkey's own reserves, and decrease in dependency for supplying fuel are possible by briquetting process, which is one of the most efficient process in reducing the conversion of coal to dust. By taking into account that fossil energy sources are happen to be consumed, and Turkey has a high potential of biomass energy, which is one of the renewable energy sources, briquetting the mixture of coal dusts and biomass may prolong the time required for reserves to be finished.

In this study, a lignite sample from Çorum–Bayat area of Turkey was briquetted at different conditions (i.e. briquetting pressure, biomass type and content, briquetting time, or binder type), and compressive strength, impact strength, and water resistance of the obtained briquettes were measured in order to determine optimum conditions for producing durable briquettes. According to the experimental findings, it was found that an increase in briquetting pressure from 350 MPa to 700 MPa was more effective than increasing it from 700 MPa to 1000 MPa with respect to three quality parameters of the briquettes manufactured from lignite or biomass samples.

On the other hand, addition of hazelnut refuse, grape TSR waste, or locust TSR waste into the lignite improved compressive strength and impact strength of the formed biocoal briquettes, and reduced water resistance of the produced biocoal briquettes. However, opposite effects were seen in the case of adding mulberry TSR waste into the lignite.

Besides, addition of molasses reduced compressive strength, impact strength (excluding the hazelnut refuse containing biocoal briquettes), and water resistance of the formed biocoal briquettes. Withal, using linobind as a binder material improved compressive strength (except for the locust TSR waste containing biocoal briquettes) and water resistance of the produced biocoal briquettes. However, its effect on impact strength varied due to the type of biomass. By the same token, adding plant root solution enhanced impact strength (excluding the locust TSR waste containing biocoal briquettes) and water resistance of the formed biocoal briquettes, and decreased compressive strength of the produced biocoal briquettes (except for the mulberry TSR waste containing biocoal briquettes).

Moreover, the hazelnut refuse biobriquettes and the grape TSR waste biobriquettes prepared under briquetting pressures of 700 and 1000 MPa, and the 20 wt% hazelnut refuse containing biocoal briquettes manufactured under a briquetting pressure of 700 MPa met with the requirements of TS 12055 for class I briquettes in terms of compressive strength and impact strength, whilst compressive strength and impact

strength of the 4 wt% linobind added biocoal briquettes produced with a lignite:hazelnut refuse ratio of 80:20 (wt%) under a briquetting pressure of 700 MPa were accordance with the limitations of TS 12055 for class II briquettes. Since these briquettes were lack of resistance to water, some further researches can be carried out to fulfill the requirements of the standards.

KÖMÜR – BİYOKÜTLE KARIŞIMLARININ BRİKETLENMESİ

ÖZET

Türkiye’deki linyit kömürlerinin büyük çoğunluğu tozlaşma eğilimindedirler. İnce taneli ve toz haldeki kömürlerin yanmadan bacadan atılmaları ve taşınmaları ile depolanmaları esnasında karşılaşılan sorunlar nedeniyle, bu kömürlerinin çoğu ızgaralı soba ve kalorifer kazanlarında yakılmaya elverişli değildir. Bundan dolayı, linyitlerin evsel yakıt olarak kullanımları sınırlıdır. Ancak, bu kömürlerin yakılmaları sırasında ortaya çıkan sorunların giderilmesi yoluyla enerji kaynaklarının temininde öz kaynakların kullanılması ve dışa bağımlılığın azaltılması mümkündür. Kömürlerdeki tozlaşma eğiliminin azaltılması amacıyla uygulanabilecek en etkin yöntemlerden birisi briketleme işlemidir. Fosil enerji kaynaklarının yakın bir gelecekte tükenecek olduğu gerçeği ve yenilenebilir enerji kaynaklarından birisi olan biyokütle enerjisi açısından Türkiye’nin sahip olduğu yüksek potansiyel göz önüne alındığında; toz haldeki kömürlerin biyokütle ile karıştırılarak briketlenmesinin, kömür rezervlerinin daha uzun süre kullanılabilmesine olanak sağlayacağı da görülmektedir.

Bu çalışmada, Çorum–Bayat linyit yataklarından çıkarılan kömür, standartlara uygun ve sağlam briketlerin üretildiği en uygun şartların belirlenmesi amacıyla, farklı çalışma şartlarında (briketleme basıncı, biyokütle çeşidi ve derişimi, briketleme süresi, bağlayıcı çeşidi) briketlenmiş ve üretilen briketlere kırılma sağlamlığı, düşme sağlamlığı, suya dayanıklılık testleri uygulanmıştır. Elde edilen deneysel bulgulara göre; briketleme basıncının 350 MPa’dan 700 MPa’a çıkarılmasının, 700 MPa’dan 1000 MPa’a çıkarılmasından daha etkili olduğu görülmüştür.

Ayrıca, linyite çotanak, üzüm pekmezi posası atığı ya da keçiboynuzu pekmezi posası atığı ilave edilmesi, oluşan biyokömürbriketlerinin kırılma ve düşme sağlamlıklarını geliştirmiş; suya dayanıklılıklarını ise, azaltmıştır. Buna karşın; dut pekmezi posası atığının ilave edilmesi durumunda, bunun tam zıttı etkiler gözlenmiştir.

Diğer yandan, biyokömürbriketlerine melas ilave edilmesi, oluşan briketlerin kırılma sağlamlıklarını, düşme sağlamlıklarını (çotanak içeren biyokömürbriketleri hariç) ve suya dayanıklılıklarını azaltmıştır. Bağlayıcı olarak linobind kullanılması ise, oluşan biyokömürbriketlerinin kırılma sağlamlıkları (keçiboynuzu pekmezi posası atığı içeren biyokömürbriketleri hariç) ile suya dayanıklılıklarını geliştirirken; düşme sağlamlığı üzerindeki etkileri biyokütle çeşidine göre farklılık göstermiştir. Bitki kökü çözeltisi ilave edildiği durumlarda ise, elde edilen biyokömürbriketlerinin düşme sağlamlıkları (keçiboynuzu pekmezi posası atığı içeren biyokömürbriketleri hariç) ile suya dayanıklılıkları artmış; kırılma sağlamlıkları (dut pekmezi posası atığı içeren biyokömürbriketleri hariç) azalmıştır.

Ayrıca, 700 ve 1000 MPa’da hazırlanan çotanak ve üzüm pekmezi posası atığı biyobriketleri ile 700 MPa briketleme basıncı altında, ağırlıkça %20 çotanak içeriğinde üretilen biyokömürbriketleri, TS 12055’de 1. Sınıf briketlerin kırılma ve

düşme sağlamlıkları için belirtilen değerlere uygunluk gösterirken; ağırlıkça %4 linbind ilave edilerek 700 MPa'da 80:20 (ağırlıkça %) linyit:çotanak oranı ile hazırlanan biyokömürbriktleri ise, kırılma ve düşme sağlamlıkları açısından 2. Sınıf briktlerle karşılaştırılabilir olarak belirlenmiştir. Ancak, bu briktlerin suya dayanıklılıkları yetersiz olduğundan; standartları sağlaması için daha ileri çalışmalar yürütülebilir.

1. INTRODUCTION

Energy is one of the most important necessities of human beings. Due to growths in population and industry, energy demand has increased, which resulted in requirement to use of present fuels more efficiently and to find alternative energy sources.

Energy sources can be classified into two main groups as nonrenewable and renewable energy sources. The former contains fossil fuels (i.e. anthracite, lignite, bituminous coal, petroleum, natural gas, asphaltite) and nuclear energy, whereas the latter consists of hydraulic, solar, geothermal, wind, wave and biomass energies.

Among fossil fuels, coal has the biggest reserves in Turkey, and the highest share of the coal reserves belongs to lignite, which corresponds to approximately 12.3 billion tons [1]. However, some of the Turkish lignites tend to be dusty, and the formed dusts can easily be transferred into ground water leading to environmental problems as well as economical ones. By briquetting process, elimination of these problems can be achieved [2]. To improve some quality properties of different coals such as calorific value, water resistance, thermal shock resistance, and transportation and storage properties, briquetting has been commonly used in many countries [3].

Of the alternative energy sources, biomass has a great potential as a result of being renewable in contrast to fossil fuels. Biomass can store some of the solar energy as a mass in its body by photosynthesis, and this energy is released during combustion of biomass [4]. However, transportation, storage, and utilization of the biomass are very difficult due to its uneven, fluffy, and dusty characteristics [5]. Therefore, direct combustion of biomass is not practical.

Co-firing biomass with coal has been an attractive way to increase the usage of biomass energy and to upgrade properties of low rank coals [6–7]. Nevertheless, density difference between coal and biomass causes some difficulties during the co-firing process [5], and this problem can be solved by densification of biomass into biomass-coal briquettes (biocoalbriquettes) [6]. By densification process, biomass materials can easily be adopted in direct combustion or co-firing with coal,

gasification, and in other biomass-based conversions as a result of their uniform shape and sizes [8].

Hazelnut refuse is an agricultural residue that stays in the field after the harvest of hazelnut, and can not be evaluated properly. Handling, storage, and utilization of the hazelnut refuse are very difficult in its original form because of its lower bulk density. By the same token, thick syrup residuum (TSR) waste is an industrial waste in the form of solid, which remains at the end of the extraction process, and needs to be eliminated from the plant. Therefore, use of hazelnut refuse or TSR waste as biomass sources and briquetting of lignite–biomass blends would be a good solution for the limitations related to coal and biomass materials.

In this study, a lignite sample from Çorum–Bayat area of Turkey, which is one of the Turkish coals tend to form dust owing to its soft characteristic, was briquetted by blending it with these biomass samples. By this way, the low grade lignite can be converted into a compact and stable fuel. However, it is very difficult to obtain strong briquettes from lignite–biomass blends without any binder material. For this purpose, molasses (a by–product of sugar extracting process), linobind (a starch–based solution) and plant root solution (a solution prepared from roots of a silvatic plant in water) were used as binders.

2. COAL

2.1 Introduction to Coal

Coal is a combustible, sedimentary, organic rock, which is composed mainly of carbon, hydrogen and oxygen. It can also be defined as the altered remains of prehistoric vegetation that originally accumulated in swamps and peat bogs [9].

With the effect of tectonic movements, the swamps and the peat bogs, in which the prehistoric vegetation was located, were buried to great depths, and the plant material was exposed to high temperatures and pressures, which induced physicochemical changes in the structure of the vegetation. Thus, coal formation started during the Carboniferous Period, which is known as the first coal age that spanned 360 to 290 million years ago, with the transformation of the plant material into peat by these physicochemical changes [9].

The peat firstly converted into lignite (known as brown coal), which is quite soft and has a color in the range of dark black to various shades of brown. The peat and the lignite are coal types with low organic maturity, which represents the measurement of the quality of each coal deposit due to temperature, pressure, and length of time in formation. However, further changes occurring in the structure of the lignite with the continuing effects of temperature and pressure over many more million of years increased its organic maturity progressively, and sub-bituminous coals were formed. Under the right conditions, these further changes carried forward the progressive increase in the organic maturity to form bituminous coals (known as hard coal), which were harder and blacker, and finally anthracite [9].

2.2 Classification of Coal Types

Coal is classified into two main groups (see **Figure 2.1**) due to rank of the coal, which refers to the degree of alteration (or metamorphism) occurring as coal matures from peat to anthracite (known as coalification) [10–11].

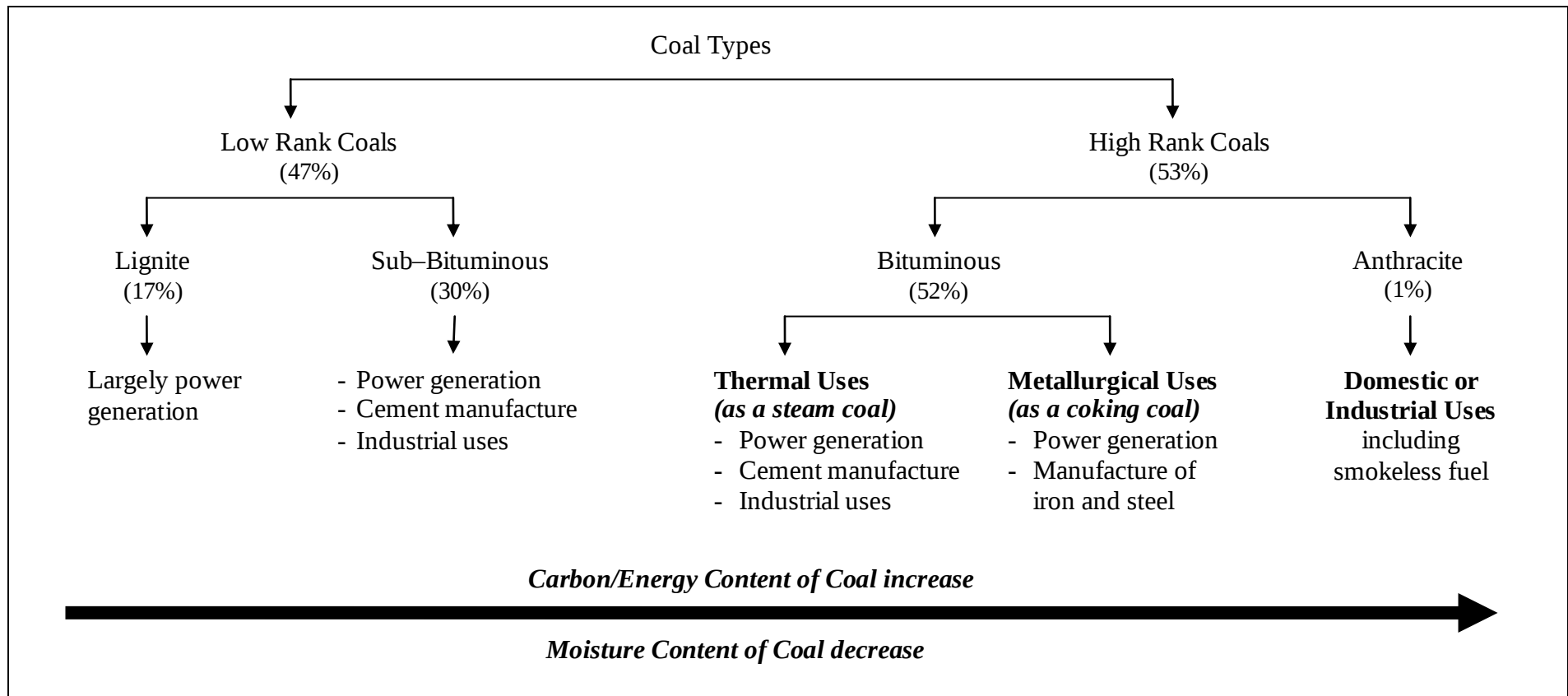


Figure 2.1 : Types of coals, their share in the World reserves, and their applications [9].

Low rank coals are typically softer and friable materials with a dull and earthy appearance. Also, they have low energy content owing to their high moisture contents and low carbon contents. Contrarily, high rank coals are generally harder and stronger materials with a black and vitreous luster. They are characterized by low moisture content and high carbon content. Therefore, their energy contents are higher than that of the low rank coals [9].

Low rank coals are divided into two groups as lignite and sub-bituminous coal due to carbon content of the coals. The lignite contains 25–35% carbon, whereas the sub-bituminous coal includes 35–45% carbon. Similarly, high rank coals are categorized as bituminous coal and anthracite with respect to their carbon contents. The bituminous coal contains 45–86% carbon, whilst the anthracite includes 86–97% carbon [10].

Generally, all low-rank coals are classified as low-grade coals owing to their high moisture contents and low calorific values. Anthracites and semi-anthracites are also categorized as low grade coals due to problems related to ignition and burnout. Summarily, coals that have at least one problem, which causes troubles during their utilization, such as low heating value or high moisture content leading to low efficiency, low volatile matter content associated with flame stability, high ash content causing ash problem and low efficiency, high sulfur content leading to high SO₂ emissions and high emission reduction costs, low ash fusibility having potential to slagging, high alkali/alkaline content having potential to fouling and slagging, low Hardgrove Grindability Index (HGI) resulting in high milling power consumption, can be called as low-grade coal [11].

2.3 Limitations of Coal

Coal is found nearly in every region of the world, especially in sedimentary rock basins, typically sandwiched as layers called beds or seams between layers of sandstone and shale [11]. The biggest reserves are located in the USA, Russia, China, and India. Its proven reserves have been estimated to be over 984 billion tons in the World [9].

In Turkey, there are approximately 1.3 billion tons of bituminous coal and 12.3 billion tons of lignite reserves. The lignite reserves are located almost every region of

the Turkey. 76% of the Turkish lignites are used for power generation, whereas 10% of these lignites are utilized as a basic energy source in many industries such as cement and sugar. On the other hand, rest of the lignite is consumed to be household fuel [10].

Despite the significant geostrategic advantage of the coal in comparison with crude oil and natural gas, direct combustion of the low-grade coals generally causes lower efficiency and higher greenhouse gas emissions, and thus, requires higher operating costs. Since all fossil fuels will eventually run out, it is essential to use them as efficiently as possible. Hence, these coals should be upgraded in terms of moisture, ash, and/or other trace elements, and should be converted into fuels that have acceptable energy efficiency and environmental security. Major techniques applied for enhancing coal properties have been blending, drying, cleaning (removal of minerals), chemical upgrading, and briquetting. These techniques provide removal of excess water and elimination of undesired organic and/or inorganic matters from the coal [11].

3. BIOMASS ENERGY

3.1 Introduction to Biomass Energy

Biomass energy is obtained from the release of heat during decomposition of the material to its elementary molecules, which represents a faster and renewable imitation of the natural processes [12]. Various definitions have been made for biomass materials [13–15].

- Biomass materials are all the living matters on Earth.
- Biomass materials are the plant matters generated by photosynthesis with the conversion of water and CO₂ into organic matters.
- Biomass materials are all the organic materials that stems from plants (including algae), trees, and crops.
- Biomass materials are all the materials derived from growing plants, or animal manure, which is a processed form of plant materials.
- Biomass materials are all types of organic substances of plant or animal origin, which are suitable for combustion.
- Biomass materials are all the matters produced directly or indirectly as a result of plant growth.

3.2 Classification of Biomass Energy Sources

There are lots of biomass energy sources that vary throughout the world. These sources can be divided into four groups such as agricultural–based biomass, forestry–based biomass, energy crops, and wastes [16]. Mainly, agricultural residues, fuel wood, charcoal, and dung are used as biomass fuels [12].

3.2.1 Agricultural–based biomass

Agricultural–based biomass can be defined to be a biomass energy source that contains agricultural crops and residues. Agricultural crops such as sugar cane, corn

(maize), wheat, sorghum, and vegetable oil bearing crops (e.g. sunflower, rapeseed (canola), and soybean) have been used to produce liquid fuels (i.e. biodiesel) [12]. However, utilization of these crops as the energy source competes with other industries (e.g. food industry).

On the other hand, agricultural residues are by-products of agricultural systems such as straws, husks, shells, and stalks. These residues can either be crop residues remained in the field after harvest (i.e. cotton stalk), or by-products of crop processing industry (e.g. rice husk) [17]. They are usually ploughed back into soil, burnt, or grazed by stock in the case of not being used for energy. However, they can be utilized in the solid fuel production. Generally, rice husk, sugar cane fiber (bagasse), coconut husk and shell, palm oil fiber, groundnut shell, and cereal straw have been utilized as energy sources [12].

Agricultural residues have been most promising choices, since they are free or almost free, indigenous, environmental friendly and abundant energy sources. However, they are bulky, heterogeneous, and have low energy density, which lead some obstacles during their storage, transportation, and utilization. By using briquetting technology, these problems can be prevented [18].

3.2.2 Forestry-based biomass

Forestry-based biomass can be described as a biomass energy source that includes forestry crops and residues. Forestry crops can be described as biomass energy sources, which mainly consist of wood. Wood has become a significant renewable energy source all over the world, and trees that grow rapidly and are suitable for coppicing are best sources of the woods (Coppicing consists of two stages that follows each other subsequently within 2–5 year periods: harvesting the tree and sprouting from the harvested stump stages.). It can be burnt as a solid fuel or used in charcoal production. However, extensive utilization of wood from natural forests can cause deforestation as well as serious ecological and social problems [12]. To avoid that, its usage has been restricted in some countries such as Cuba [19].

On the other hand, forestry residues are by-products of forested systems such as sawdust, off-cuts, bark and woodchip rejects. These residues are generally left to rot on site without used for any purpose. However, it is possible to collect these residues for the purpose of solid fuel production [12].

3.2.3 Waste

Wastes can be defined as biomass energy sources that consist of animal waste, sewage, industrial waste, and municipal solid waste. Animal waste includes manures from farm animals such as pigs, chickens, and cattle. These manures had been used as fertilizer. However, environmental constraints on odor and water pollution resulted in requirement to waste management practices. By using anaerobic digestion, these wastes can be used for producing gaseous fuels. Similarly, sewage can be used to obtain gaseous fuel by anaerobic digestion. Besides, biogas or bio-oil production can also be carried out by incineration or pyrolysis of the remained sewage sludge [12].

On the other hand, industrial waste contains residues or by-products of the industrial plants in the form of solid (i.e. peelings and scraps from fruits and vegetables, pulp and fiber from sugar and starch extraction, filter sludge, coffee grounds, and food that does not have quality properties in accordance with standards), or liquid (e.g. waste streams from meat, fruit and vegetable washing, fruit and vegetable blanching, meat, poultry and fish pre-cooking, and wine making processes). Elimination of wastes related to industrial plants has been a problem for companies. However, solid wastes can be used as solid fuel, whereas liquid wastes can be utilized for the production of gaseous and liquid fuels via anaerobic digestion and fermentation, respectively [12].

By the same token, municipal solid waste represents total waste excluding agricultural waste, sewage sludge, and industrial waste. It contains both benign and very toxic wastes, and its composition varies due to location and the type of the collection. It can either be undergone direct combustion or anaerobic digestion [12].

3.3 Advantages of Biomass Energy

Coal and biomass both consist of same basic components. However, proportions of these components are different. Therefore, combustion behaviors of both materials are different. For instance, biomass comprises almost four times more oxygen besides its less sulfur and nitrogen contents, which lead to having higher volatile matter content and higher reactivity in comparison with coal [15]. Thus, it shows

superior ignitability and combustibility characteristics with higher burning rate compared to coal [17, 20].

On the other hand, air pollution emissions such as sulfur and nitrogen oxides, which cause acid rains and ozone depletion, are released to the atmosphere during the combustion of coal [13, 17, 21]. However, biomass does not contribute to SO₂ emissions owing to its negligible sulfur content [12]. Moreover, greenhouse gas emissions (i.e., CO₂, CH₄, etc.) are also released to the atmosphere during coal combustion that leads to global warming, whereas biomass releases the same amount of CO₂ during combustion as is consumed during growth. Hence, biomass aids recycle of atmospheric CO₂ and does not take a share in greenhouse gas production. Thus, it is called as CO₂-neutral fuel. Furthermore, mixing coal with biomass materials reduces fossil-based CO₂ emissions [13, 17, 21].

Additionally, biomass materials produces small amounts of ash (0.5–12.5%) in comparison with coal, and ash of biomass materials can be used as fertilizer in order to recycle potassium and phosphorus elements in the ash structure, since it does not include any hazardous substances [12, 15].

Besides, biomass is an indigenous source in contrast to petroleum and natural gas. Therefore, it is not influenced from the world price fluctuations or the supply uncertainties of imported fuels [12, 14]. Withal, it provides decrease in dependency to foreign oil, and enhances energy and economical security [13].

Also, utilization of agricultural and forestry residues, and municipal solid waste as the biomass energy sources is an effective way of recovering waste materials. Thus, it decreases problems related to waste elimination [12].

3.4 Limitations of Biomass Energy

Biomass has lower bulk density compared to coal owing to its high moisture exceeding 50% [12, 15]. This results in requirement to special boilers or dewatering/drying processes, since traditional boilers require moisture content to be below 15% [15]. Withal, microorganisms can easily grow on biomass materials, which shorten storage time and decreases fuel quality, in the case of high moisture content [8]. Consequently, transportation, storage and handling of biomass materials are more difficult and more expensive than that of coal [12, 15, 22].

Biomass has also much higher alkaline (especially potassium), calcium, phosphorus, and in the case of straw, leaves and wood bark, chlorine contents than coal. High content of alkaline and chloride may lead to corrosion and accumulation of sediments on the surface of boilers during combustion. Besides, softening temperature of ash from biomass (750–1000°C) is lower than that of coal ($\geq 1000^\circ\text{C}$), which also results in fouling and slagging problems related to faster accumulation of sediments on the boiler surface during combustion of biomass compared to combustion of coal [15, 17].

Additionally, source competition between biomass energy and other fields (i.e. food industry) and seasonal availability of biomass materials introduce some limitations as well as political and institutional constraints (e.g. energy policies, taxes, and subsidies) into utilization of biomass materials as fuel [12, 22].

4. BRIQUETTING

4.1 Introduction to Briquetting Process

Briquetting is simply a densification process with the application of pressure to useless fuel materials in order to obtain a compact, durable, and high quality fuel [23]. Briquetting process (see **Figure 4.1**) consists of drying, grinding, sieving, compacting, cooling, and packing stages. During these stages, moisture content of raw material is eliminated; the dried material is ground, passed through a screen, and briquetted; obtained briquettes are cooled and packed, respectively [24–25].

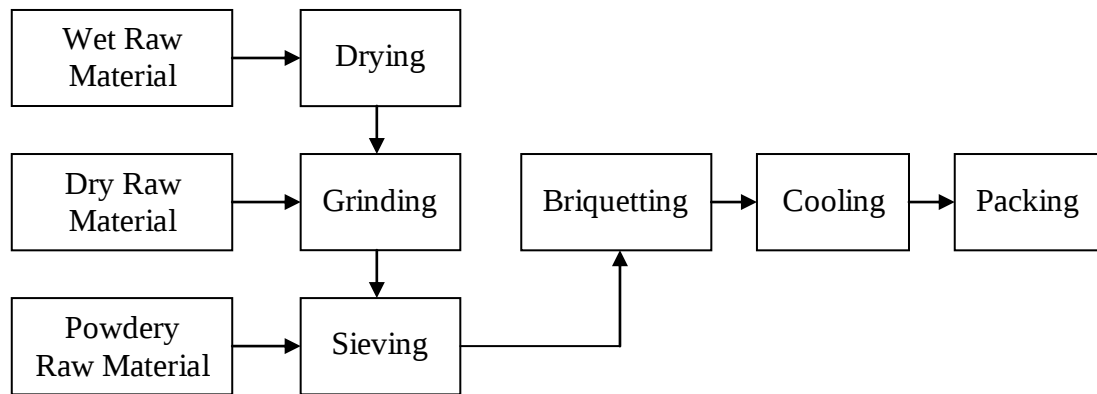


Figure 4.1 : Flow diagram of briquette production process [25].

Briquetting is one of the promising methods for manufacturing a uniform, stable and durable fuel with the standard quality [26–27]. By briquetting process, the costs of handling, transportation, and storage can be reduced, and volumetric calorific value can be increased owing to increase in bulk density and decrease in moisture content [8, 25–27]. Moreover, briquettes with the self–desulphurization and the self–denitrification characteristics can be obtained by adding some additives into briquette formulations. Hence, no extra apparatus is required for reduction in emissions, which results in reduction in operating and investment costs [28]. Pollution from total suspended particles is also prevented by briquetting process [29].

Briquetting process can either be carried out at room temperature (cold briquetting) or at elevated temperatures (hot briquetting) with or without using a binder material, and obtained briquettes can either be utilized for the household or the industry [30].

Briquettes can be produced from biomass materials in three different ways as seen in **Figure 4.2**. One kind of biomass or mixtures of various biomass materials can be used in the biomass-based briquette production [30].

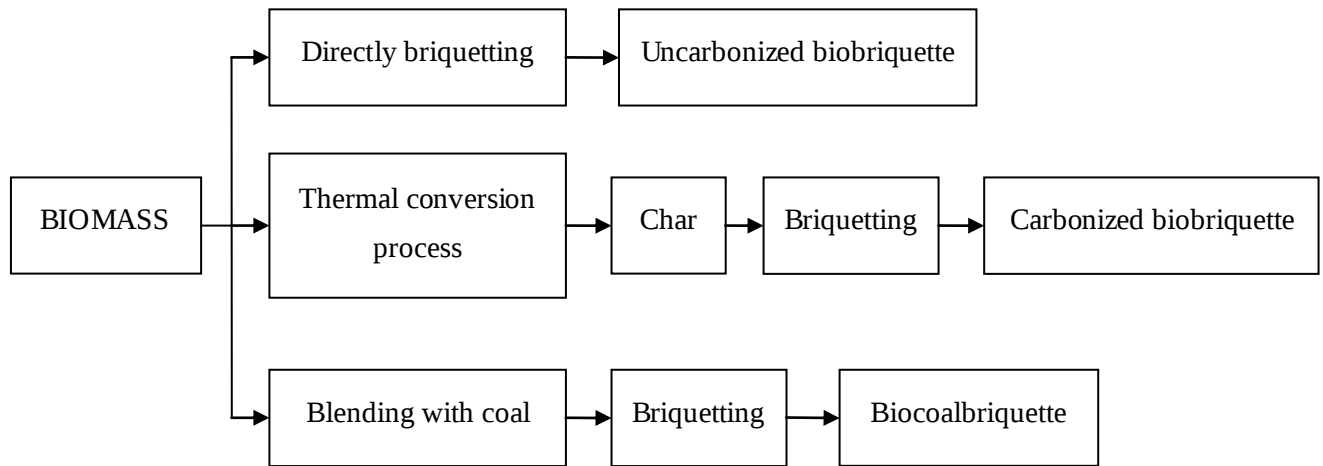


Figure 4.2 : Production methods of biomass-based briquettes [30].

Biocoal briquette represents a type of solid fuel produced from coal and biomass with the application of pressure. During the briquetting process, biomass and coal particles adhere and interlace to each other. Therefore, these two materials do not separate from each other during storage, transportation and utilization [31].

During combustion process, coal acts as a stabilizer in the mixture of coal and biomass, whilst biomass reduces SO_2 , NO_x and CO_2 emissions owing to its low sulfur content, low nitrogen content, and CO_2 -neutral characteristic, respectively [15]. Besides, ignition and fuel properties of the coal can be improved with the addition of biomass by virtue of lower ignition temperature of biomass [31]. Moreover, rate of coal consumption can also be decreased [28].

However, selection of the biomass material should be carried out carefully considering limitations associated with the utilization of biomass energy. Some of the biomass properties preferred for briquetting are given below [24–25, 32]:

- Moisture content should be in the range of 10–15% in order to prevent requirement to more energy consumption for drying, and problems appeared during grinding. Moreover, high moisture content causes decrease in combustion temperature that leads to quality of combustion reaction and reaction products.
- Ash content should be less than 4%, since slagging behavior of the fuel is influenced from ash content, together with furnace temperature and mineral composition of the ash.
- Flowing characteristics that allow flow of the material in conveyors, bunkers, and silos are preferred for briquetting. These characteristics are significantly influenced from particle shape and size of the material. Since granular and homogenous particles with size of 6–8 mm can easily flow in conveyors, bunkers, and silos, they are suitable for briquetting process.

4.2 Binding Mechanisms

The strength and durability of the briquettes depend on the physical forces that bind the particles together. These binding forces have been divided into five major groups as solid bridges, attraction forces between solid particles, mechanical interlocking bonds, adhesion and cohesion forces, and interfacial forces and capillary pressure [8].

Ellison and Stanmore [33] stated that molecular forces and hydrogen bridges were responsible for the formation of the briquettes. They also mentioned about the presence of some evidences related to covalent bonds that may also act role on the briquette formation at elevated temperature, which was indicated not to be proven.

4.2.1 Solid bridges

Solid bridges may be formed by diffusion of molecules from one particle to another at the points of contact due to the application of high pressures and temperatures. Solid bridges may also be developed due to crystallization of some ingredients, chemical reaction, hardening of binders, and solidification of melted components [8].

4.2.2 Attraction forces between solid particles

Since the particles are brought close together during the compression process, solid particles can be resulted to adhere to each other due to short range forces such as molecular (i.e. valance forces, hydrogen bridges, and van der Waals forces), electrostatic, and magnetic forces [8].

4.2.3 Mechanical interlocking bonds

Mechanical interlocking bonds can develop via fibers, flat-shaped particles, and bulky particles that could interlock or fold about each other [8].

4.2.4 Adhesion and cohesion forces

Highly viscous binders such as molasses and tar adhere to the surfaces of solid particles to generate strong bonds that are very similar to those of solid bridges, whereas presence of liquids such as free moisture between particles results cohesive forces between particles [8].

4.2.5 Interfacial forces and capillary pressure

Thin adsorption particles (>3 nm thick), which are immobile, can form strong bonds between adjacent particles either by smoothing out surface roughness and increasing the inter-particle contact area or by decreasing the inter-particle distance and allowing the inter-molecular attractive forces to participate in the bonding mechanism [8].

4.3 Quality Parameters of Briquettes

The quality of the products must meet requirements of the consumer and standards of the market. Therefore, the products must withstand the rigors of handling, transportation and storage. The forces causing damage during handling, transportation and storage can be classified as compression, impact and shear forces. The effectiveness of the inter-particle bonds has been measured in terms of strength and durability via compressive, abrasive, impact, and water resistances of the briquettes. The types of the physical quality tests should be selected by taking account of the way that products were handled, transported, stored, and utilized in order to obtain an approach on the production of fragments and fines, approximately.

Estimating the amount of damage in terms of strength and durability can help optimization of the feed material and the procedure, and can help develop strategies for improving the quality of the products [8].

4.3.1 Compressive resistance

Compressive resistance (or crushing resistance or hardness) is the maximum crushing load a briquette can withstand before cracking or breaking, which simulates the compressive stress due to weight of the top pellets on the lower pellets during storage. This resistance indicates the quality rapidly, although it does not represent a measure of the dusting potential of the products during handling, transportation, and storage [8].

Compressive resistance of the products is determined by a test, in which a single briquette is placed between two flat, parallel plates that have greater facial areas than the area of the briquette and an increasing load is applied at a constant rate until the briquette is cracked or broken. The load at fracture is reported as force or stress [8].

4.3.2 Abrasive resistance

Abrasion is caused by shearing forces at edges and surfaces of the briquettes. Therefore, abrasive resistance (or durability) simulates handling of the products either mechanically or pneumatically. The durability has been measured by tumbling can, Holmen tester and Ligno tester methods [8].

The tumbling can method, which simulates mechanical handling of the briquettes, is used for predicting fine production due to mechanical handling. In this method, 500 g of sample is tumbled for 40 min at 60 rpm, and fines, which are produced from sample due to impact, and shearing of briquettes over each other and over the wall of the tumbling can, are sieved using a sieve size of about 0.8 times of the product diameter. The durability is estimated as the ratio of weight after tumbling over the weight before tumbling, multiplied by 100 [5, 34].

The Holmen tester method simulates pneumatic handling of the briquettes. In this method, 100 g of sample is circulated pneumatically through a square conduit of pipe or tubing with right-angled bends for 30–120 s, and the remaining particles are sieved using a sieve size of about 0.8 times of the product diameter [35].

The Ligno tester method, which is an adapted form of an Austrian standard test method, is the fastest method compared to the former and the latter methods. In this method, 100 g of sample is circulated using an air stream of 70 mbar for 60 s around a perforated chamber that was an inverted square pyramid with perforated sides, and the percentage of fines that passed through a 3.15 mm sieve is taken as the measure of the durability, while fines are being removed continuously during the test [36]. This method was reported to be more sensitive to durability influencing factors (i.e. adding binder) than other methods [37]. However, it was also stated that its repeatability and reproducibility were lower compared to the tumbling can method [38].

4.3.3 Impact resistance

Impact resistance (or drop resistance or shatter resistance), which is caused by impact forces that resulted in shattering both on the surface of the briquettes, and along any natural cleavage planes of the briquettes, simulates the forces encountered during transportation of the products from trucks onto ground, or from chutes into bins [8].

To estimate impact resistance of the briquettes, various test methods have been used by researchers. Sah et al. [39] applied a test method, in which briquettes were subjected to four repeated drops from 1.85 m height onto a metal plate, and the percentage of retained weight was determined, whereas briquettes with a diameter of 50 mm and a thickness of 18 mm were dropped from 1 m height onto a concrete surface 10 times, and the percentage of lost weight was calculated in the method used by Lindley and Vossoughi [40].

Briquettes were also subjected to two repeated drops from 1.83 m height onto a concrete surface according to ASTM method D440–86 [41], and impact resistance index (IRI) was obtained by using Eq. (4.1), in which N represents the number of drops, and n refers to the total number of pieces after N drops [42]. In the calculation, pieces weighing less than 5% of the original weight were assumed to be ignorable, and minimum acceptable value of IRI was suggested to be 50 by Richard [42]. On the other hand, Raghavan and Conkle [43] proposed that briquettes remaining intact after dropping both from 0.3 m and 1.5 m onto a concrete floor to be taken as acceptable.

$$IRI = \frac{100 \times N}{n} \quad (4.1)$$

Gürbüz–Beker [44] determined impact resistance according to ISO–R616 method, in which briquettes were subjected to repeated drops from 1.80 m height onto a steel plate until all the pieces passed through a 20 mm sieve, and the sum of percentages of over sieve pieces was taken as shatter index (SI). Minimum acceptable value was informed to be 2000.

4.3.4 Water resistance

Water resistance simulates short-term exposure to rain or high humidity conditions during transportation and storage [8]. To estimate water resistance of the briquettes, various test methods have been used by researchers. Lindley and Vossoughi [40] applied a method, in which briquettes with a diameter of 50 mm and a thickness of 18 mm were immersed in water at 27°C for 30 s, and the percentage of absorbed water was taken as water resistance. Richards [42] suggested that maximum water absorption should not exceed 5% of original weight of the briquettes by using the similar method.

4.3.5 Combustion characteristics

Combustion is a very complex, heterogeneous, oxidation reaction, which is a function of temperature [45]. It consists of two stages, in which volatile matter mainly evolves and burns prior to char combustion. In the former stage, briquetting pressure has no effect on the rate of reaction, and the reaction rate constant and its order vary linearly with the fuel ratio, whilst coal type and briquetting pressure (up to a threshold pressure value) significantly affect the rate of reaction due to different ash layer porosity, and the reaction is controlled by oxygen diffusion through both the gas boundary layer film and the ash layer, in the latter stage. The combustion behavior may be simulated by volume model and shrinking core reaction model in the former and the latter stages, respectively [46–47].

Combustion characteristics of fuels can be classified as macroscopic (i.e. ultimate analysis, heating value, moisture content, particle size, bulk density, and ash fusion temperature) or microscopic (e.g. thermal, chemical kinetic, and mineral data)

properties. It can also be divided into four groups as physical, chemical, thermal, and mineral properties [48].

- Physical properties are related to commodity (i.e. density, porosity, and internal surface area), or fuel preparation methods (e.g. bulk density, particle size, and size distribution).
- Chemical properties are ultimate analysis, proximate analysis, higher heating value, analysis of pyrolysis products, heat of pyrolysis, heating value of the volatiles, and heating value of the char.
- Thermal properties are specific heat, thermal conductivity, and emissivity, which depend on moisture content, temperature, and degree of thermal degradation.

Understanding combustion properties of the fuel provides maximizing efficiency of combustion, minimizing carbon particle emissions, and determining design parameters of combustion parameters [49]. For instance, particle size sets the burnout time of the fuel, whereas size distribution controls the form of the flame. On the other hand, moisture, ash content and calorific value are the main factors influencing fuel cost [50]. Similarly, Tabares et al. [51] stated that combustion behaviors of briquettes can be modified via conditions of manufacturing (especially diameter) and selection of raw material (especially fixed carbon).

Evaluation of suitability of fuel for chosen combustion way and optimization of efficiency can be done by estimating emittance of heat, loss of moisture, loss of volatiles, oxidation of fixed carbon, or identification of product gases via thermal analysis methods such as thermogravimetry/ differential thermogravimetry (TG/DTG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), effluent gas analysis (EGA), and thermal analysis complemented with Fourier Transform Infrared spectroscopy (TG–FTIR). By using these methods, reaction profiles covering the whole combustion period can be obtained in the form of a graph, at which method dependent variables (e.g. temperature, heat, weight or gas compositions) are monitored, and thermal features (i.e. ignition temperature, maximum combustion rate, maximum combustion rate temperature, reaction zones, burnout temperature, residue, etc.) indicating combustion behavior of the fuel can be directly determined from the reaction profiles [45].

4.4 Factors Affecting Strength and Durability of the Briquettes

Factors related to raw materials, preconditioning processes, and densification equipment variables affect the quality of the briquettes in terms of strength and durability. Since these factors interact with each other, they should be optimized by applying optimization procedures [8].

4.4.1 Effects of feed constituents

Raw materials show different physicochemical properties due to inherent variability of the compounds present in their compositions. Since the binding behaviors of this constituents are similar regardless of the type of raw material, studying the effects of feed constituents (i.e. starch, protein, fiber, fat/oil, and so on) may be more useful. Gelatinization of starch, denaturation of protein, and solubilization and subsequent recrystallization of sugars and salt are the common binding characteristics of the constituents observed during briquetting process [8].

4.4.1.1 Starch

Starch acts as a binder. Heat, moisture, and shearing forces are reported to provide starch gelatinization, which increases binding ability of the starch, and thus, durability of the briquettes. It was also stated that addition of the pregelatinized starch resulted in briquettes with better quality in terms of hardness and durability compared to addition of native starch [8].

4.4.1.2 Protein

Protein acts as a binder. Heat, moisture, and shearing forces are reported to cause protein denaturation, which induces binding ability of the protein. It was also stated that addition of the denaturated protein resulted in briquettes with worse quality in terms of hardness and durability compared to addition of native protein [8].

4.4.1.3 Fiber

Fiber can be divided into two groups due to their solubility in water. Water soluble fibers affect structural integrity of the briquettes positively, whereas water insoluble fibers may entangle and fold between particles or fibers. Fibers may not strongly bond between fibers or particles due to their resilience characteristics (i.e. elasticity). However, by addition of chemical agents (e.g. NaOH, CaO, or urea), or by increasing

moisture content, resilience characteristics of the briquettes decrease, and thus, durability of the products increase due to degradation of cell wall structure and separation of lignin from cellulose. On the other hand, weak spots for fragmentation form in the presence of large fibers in the briquette matrix [8].

4.4.1.4 Fat/oil

Fat/oil acts as a lubricant between particles, and also, between feed and die. Since fat/oil reduce frictional forces during compression process, pressure in the die decreases, which causes decrease in the product durability. Also, binding properties of the water soluble components (e.g. starch, protein, and fiber) present in the briquette are inhibited due to hydrophobic nature of the fats/oils. Moreover, native fat presents in the cell wall is claimed to come out of the cell, and act as a binder by making solid bridges in the absence of fat addition. Therefore, added fat is reported to be introduced up to 1.5% to optimize the durability of the products [8, 35].

4.4.1.5 Lignin and extractives

Lignin acts as a binder by softening at elevated temperatures owing to its low melting point ($\sim 140^{\circ}\text{C}$), and helps binding process [8, 32]. It was stated that strength characteristics of the briquettes may be positively influenced by adhesive properties of thermally-softened lignin [27]. However, an increase in content of lignin plus extractives above 34% in wood samples was reported to result in decrease in the product durability by Bradfield and Levi [52].

During combustion of the briquettes, lignin stays in char and contributes to fixed carbon content, whilst cellulose and extractive matters play role on production of volatile matters. Volatile matters burn homogeneously and rapidly in the gaseous phase, whereas combustion of fixed carbon lasts longer. Hence, ignition temperature and maximum combustion rate decrease, and calorific value and burnout time increase with the increase in lignin content due to increase in fixed carbon content. Contrarily, opposite effects are seen, when extractive matter and holocellulose contents are increased [53].

4.4.2 Effects of feed moisture content

Water acts as a binder and a lubricant. It increases contact area between particles, which aids development of van der Waals forces. It also helps briquetting in the

presence of water soluble compounds (e.g. starch, sugar, soda ash, sodium phosphate, potassium salt, and calcium chloride) [8].

Many researches have been carried out to determine the effects of the moisture content on quality of the briquettes in terms of strength and durability. Gürbüz–Beker [44] reported that compressive and impact strengths of the briquettes produced from low-rank Afşin–Elbistan lignite with moisture content of 8–15% at room temperature and 550 MPa increased with the increase in moisture content of the feed. However, Jha et al. [54], who investigated the effect of moisture content on chopped cotton stalk briquettes in the range of moisture content of 8.5–21.45%, determined that increase in moisture content up to about 17% resulted in increase in bulk density and hardness, and decrease in resiliency, whereas above the threshold level, the trend changed to its reverse. These results showed that strength and durability can only enhance with the increase in moisture content until a threshold level [8]. The moisture content of 6–12% was found to give high quality binderless briquettes at room temperature and pressure of 34–138 MPa for all woody materials and the optimum value was reported as about 8% by Li and Liu [5].

It was proposed that complete flattening and the release of natural binders from particles may be prevented at elevated moisture levels, since moisture trapped within the particles owing to its incompressibility [55]. Moreover, excess particle to particle lubrication causing heterogeneous compression, and thus, lower durability, was observed by Winowski [56] due to remaining of water on the surface of particles in the presence of high fiber content, which can not absorb moisture. On the other hand, the higher the water to starch ratio, the higher the durability as a consequence of enhanced starch gelatinization [8]. Minimum water to starch ratios was postulated to be 0.3:1 and 1.5:1 for initiation and completion of gelatinization, respectively, by Lund [57].

4.4.3 Effects of feed particle size

Since moisture absorbing capacity of the fine particles is higher and large particles are fissure points causing cracks or fractures, durability increases as particle size decreases [8]. Singh and Kashyap [58] showed that durability of the briquettes produced from rice husk with a molasses content of 25% at 31.2 MPa pressure increased from 84.1% to 95% as the average particle size decreased from 5.14 mm to

4.05 mm. However, grinding increases manufacturing costs. Thus, a mixture of different particle sizes may provide better quality, which can also allow to interparticle bonds [8].

On the other hand, Paulrud [59] produced briquettes from wood residues (stem wood without bark), which were cut either in impact, or knife mills. Wood powder from impact mills was found to contain more fine particles than wood powder from knife mills, and particle shapes were determined to be different according to mill type. Bridging tendency of impact mill powder was reported to be higher than that of knife mill powder. It was also indicated that an increase in smaller particle content resulted in negative effect on fuel feeding, slightly increase in NO emissions, positive effect on ignition, and decrease in contents of unburned pollutants and unburned matters.

4.4.4 Effects of preheating

Elevated feed temperatures are usually preferred to activate inherent/added binders, and to promote plastic deformation of thermoplastic particles, which provides binding permanently [8]. Iyengar [60] reported that compressive strength of coal briquettes increased from 1.7 MPa to 24.0 MPa by increasing feed temperature from 30°C to 250°C, whereas compressive strength of briquettes produced from bituminous coal were determined to increase from 44.1 N to 892.4 N by increasing feed temperature from 140°C to 240°C by Komarek [61].

Sağlam et al. [62] found that preheating of briquettes produced at 80°C and 100 MPa from Yatağan, Soma and Tunçbilek lignite dusts with the addition of sulphide liquor enhanced water resistance of the products, whereas compressive strength slightly decreased. They also reported that preheating of calcium sulphide liquor containing briquettes to 320°C showed approximately similar quality properties with ammonium sulphide liquor containing briquettes, which are preheated to 240°C.

Increase in preheating temperature can be achieved either by direct heating (i.e. friction, fluidized bed heating, and steam conditioning), or by indirect heating (e.g. conduction based heating systems such as hot oil circulation heat exchangers). However, temperatures above 300°C may result in decomposition of the biomass materials [8].

Steam conditioning, which is generally carried out at 103–448 kPa for 20–255 s, promotes the activation of the natural or added binders, and the reduction of germ

and bacterial counts. It also provides bond formation between particles via capillary sorption, and physicochemical changes (e.g. thermal softening, starch gelatinization, and protein denaturation) owing to condensation of the steam resulting in a thick film around the particles [8].

Conditioning with low pressure steam (i.e. high heat and high moisture) was found to enhance quality of the briquettes produced from formulations with high starch content, whereas quality of the briquettes produced from formulations with high protein content were stated to be better by conditioning with high pressure steam (e.g. high heat and limited moisture) [63–64]. Thomas et al. [65] clarified that low steam pressure is used in the case of requirement to more water (i.e. starch gelatinization), while high steam pressure is preferred for the opposite cases (e.g. protein denaturation).

4.4.5 Effects of binders

To increase quality of the briquettes, binders are added to formulations in the case of insufficient strength and durability values. A binder, which can be a liquid or solid, forms a bridge, film or matrix, or causes a chemical reaction to make strong inter-particle bonds. It is mainly selected due to its cost and environmental friendliness as well as its effects on quality [8].

Binders can be divided into two groups as chemical and biological binders. Chemical binders, which mainly contain lignosulfonate (a by product from pulp and paper mill industries) and lime, are generally added in the ratio of 0.5–5%. Whereas biological binders, which commonly consist of molasses, starch, waste paper, and saw dust, are used in the amount of 20% or more in order to achieve the same durability values with the chemical binders [8].

Many studies have been carried out on effects of binders. It was observed that durability increases with the increase in binder ratio, and there is an inverse ratio between particle size of the feed and required amount of binder addition [8].

Gürbüz–Beker [44] determined that compressive strength, impact strength, and calorific value of the briquettes produced from low-rank Afşin–Elbistan lignite at room temperature under 550 MPa pressure by adding biological binders (i.e. brewery waste, paper mill waste, sawdust, and sunflower shell) in the range of 0–20% increased, when binder ratio increased. Xu et al. [66] also reported that briquetting

performance of the coal briquettes increased as the ratio of biomass addition increased.

Singh and Singh [67] reported that durability of the briquettes produced from rice straw at a particle size of 0.15 mm under 29.4 MPa pressure either by adding 10–25% of molasses or sodium silicate, or by adding a mixture of them in equal amounts were 40–80%. Kim et al. [68] also determined that compressive strength of the bio-briquettes produced from a blend of corn stalk (20–30%) and coal (70–80%) by adding pulp black liquor (a by-product from the pulp production industry) in the range of 5–20% were increased from 0.5 MPa to 5–17 MPa. Similarly, Chin Chin and Siddiqui [69] estimated that quality and burning rates of the briquettes improved with the increase in binder content. They also stated that starch and molasses were good binders owing to their abundance and cheapness, whereas, water reported to be a better binder than molasses for rice husks. However, Taylor and Hennah [70] reported that further narrowing is prevented above a threshold level due to saturation of interstices with binder, which results in high hydrostatic pressure in the binder. On the other hand, Tang et al. [71] reported that dispersion rate of sewage sludge depends on (coal fine:sewage sludge) ratio and agitating strength during briquetting of coal fines with sewage sludge, and the higher the dispersion rate, the greater the briquette strength.

4.4.6 Effects of briquetting equipment variables

For the purpose of briquetting, roll presses are commonly used [8]. It was indicated that speed of screw feeder and roller speed, pressing force applied to per unit roller width, gap between the rollers, and system rigidity (e.g. response of the system to variations such as bulk density of the feed) were the five major parameters playing role on the performance of the roll press [72]. It was also stated that briquetting pressure is the most important parameter among other equipment variables [8].

4.4.6.1 Effects of briquetting pressure and dwell time

By applying pressure, inter-particle bonds are promoted due to squeezing inherent binders (i.e. starch, protein, lignin, and pectin) out of the particles. It was generally stated in studies that the higher the pressure, the greater the quality [8].

Li and Liu [5] investigated quality of the biobriquettes produced from sawdust (obtained from oak, pine, or cottonwood), mulch (obtained from oak or cottonwood), and bark and chips of the oak in terms of compressive, abrasive and impact resistances in the pressure range of 34–138 MPa, and concluded that quality enhanced via increase in pressure. Similarly, Jha et al. [54] investigated the effect of briquetting pressure on chopped cotton stalk briquettes in the range of 13.79–34.47 MPa for 1 min, and concluded that increasing pressure resulted in increase in bulk density and hardness, and decrease in resiliency.

Singh and Kashyap [58] reported that durability of the briquettes obtained from rice husk at an average particle size of 4.05 mm with the addition of 25% molasses increased from 80% to 90%, when pressure was increased from 7.8 MPa to 31.2 MPa. Whereas, impact resistance of the briquettes produced from pre-heated rice husk at 225°C was found to increase from 72% to 99.8% as pressure was increased from 68.6 MPa to 257.4 MPa by Shrivastava et al. [73].

Chin and Shiddiqui [69] determined that durability of the bio-briquettes increased from 27.5 N to 95.7 N for sawdust, from 1.2 N to 4.6 N for rice husk, 1.3 N to 6.7 N for peanut shell, from 10 N to 73.3 N for coconut fiber, from 10 N to 36.2 N for palm fiber with the increase in pressure from 1 MPa to 10 MPa. They also found that length expansion decreased and quality improved as briquetting pressure increased.

On the other hand, Ndiema et al. [74] mentioned about the presence of a maximum value, above which cohesion bonding of the briquettes can not be increased significantly, for biobriquettes produced in the range of 20–140 MPa. Similarly, Kim et al. [28] determined that increase in briquetting pressure up to 50 MPa enhanced mechanical strength of the biocoal briquettes, and above the threshold value, no significant effects were seen.

Chin Chin and Siddiqui [69] also observed that quality and burning rates of the briquettes improved with the increase in dwell time, and that length expansion decreased as dwell time increased up to an optimum value.

4.4.6.2 Effects of briquetting temperature

Briquetting process can be categorized as cold and hot briquetting processes due to briquetting temperature. In the former process, materials are densified into briquettes

at room temperature, whilst briquetting is carried out at elevated temperatures in the latter process.

Zhou and Zhang [75] stated that briquetting at room temperature is better than hot briquetting by the virtue of its simplicity, mobility, less investment and operating costs, and less energy consumption. They also reported that hot briquetting is very sensitive to humidity, and thus, moisture content should be in the range of 6–14% for hot briquetting systems, whereas materials with a moisture content of 8–35% can be briquetted at room temperature.

However, Taylor and Hennah [70] investigated the effects of temperature on char briquettes produced with the addition of a binder, and concluded that as temperature decreases, compaction rate reduces due to decrease in displacing rate of binder from narrowing interstices, which promotes structural flaws and decreases durability, whereas durability remains constant regardless of temperature for normal compaction rates, at which an equilibrium binder distribution is achieved.

Similarly, Tosun [76] reported that water resistance of the hot briquettes produced from lignite with the addition of magnesite binder were superior than that of cold briquettes due to softening of organic binder at elevated temperatures. However, he also indicated that cold briquetting is more advantageous in the point of financial conditions.

4.4.7 Effects of briquette shape and sizes

Shape and sizes of the briquettes are other factors that may influence briquetting characteristics. Thus, Rahman et al. [77] investigated the effect of shape and sizes of the cylindrical, ovoid, and pillow-shaped briquettes prepared from low temperature carbonization of non-caking coal by adding water and starch-based binder, and determined that surface compressive strength of the cylindrical briquettes was 10 times greater than other positions, whereas the strength of ovoid and pillow-shaped briquettes, which was found to be one-fifth of surface compressive strength of the cylindrical briquettes, were regardless of dimensions and weight. Similarly, Lu et al. [47] reported that shapes of spherical and cylindrical ($L/D=1$) biobriquettes did not significantly affect combustion behaviors in the case of having same diameter values.

On the other hand, Altun et al. [45] reported that smaller diameter and length values decreased activation energy value, and increased combustion efficiency, whereas size

enlargement had detrimental effects. Besides, it was stated that briquette geometry significantly influenced effectiveness of the combustion reaction, and combustion performance was improved as compactness of the briquettes increased (i.e. $L/D \approx 1$).

4.4.8 Effects of briquette porosity

Chow et al. [78] focused on the effect of char porosity of hot briquettes on strength, and proposed an empirical correlation (see Eq. (4.2)) obeying equation of Ryshkewitch, in which U , p , and a refer to ultimate compressive strength, total porosity, and porosity efficient (sensitive to interfacial bonding) respectively, and decrease in porosity efficient indicates penetration of binder into pores. It was also stated that strength of hot briquettes are positively affected by penetration ability of binder into submicron pores.

$$U = U_0 \times \exp \left[-a \times p \right] \quad (4.2)$$

On the other hand, Burchill et al. [79] determined that high mesoporosity of the coals briquetted with the addition of molasses resulted in greater tendency to breakage of the particles under shear stress, which caused decrease in briquetting performance.

4.4.9 Effects of post-production conditions

Strength and durability of the briquettes change due to curing time, cooling or drying processes applied after manufacturing and storage conditions.

4.4.9.1 Effects of cooling and drying processes

To provide storage safely, the excess heat and moisture should be removed from the products. It was indicated that the final temperature of the products should be within 5°C of ambient temperature, whereas the final moisture content should be less than 13%. It was also stated that cooling process promotes structural integrity owing to developed bonds between particles due to recrystallization of soluble components, and that insufficient cooling reduces the durability due to stress cracks. Moreover, cooling time of the briquettes is important as well as final temperature in order to prevent fragments caused by stress [8].

4.4.9.2 Effects of curing time and temperature

Curing time significantly influences moisture content, mechanical strength and the water resistance of the coal briquettes. For instance, hydrophobicity of the briquettes, which refers to tendency to water resistance, was indicated to be increased with the increase in curing time by virtue of aiding water evaporation and preventing re-entry of moisture [80]. Besides, the product strength measured immediately after manufacturing, which is called “green strength”, is usually different than strength of the products determined after a time period (usually a week), which is called “cured strength”. As a result of these changes, the time of measurements of quality parameters (i.e. durability) should also be reported with experimental values [8].

On the other hand, Blesa et al. [81] studied effects of curing temperature on mechanical properties of the briquettes produced from char of co-carbonization process of low-rank coal and olive stones by adding molasses and H_3PO_4 , and concluded that briquettes with adequate mechanical and water resistance properties were obtained by curing at 200°C for 2h due to carboxylic acid formation promoted either by oxidation of briquettes with the aid of temperature, and by polymerization of binder with the aid of H_3PO_4 .

4.4.9.3 Effects of storage conditions

Short-term exposure to rain or high humidity conditions is deleterious to product quality, since increase in moisture content above a threshold level results in reduction of the binding forces between particles due to increase in volumetric expansion and free water level, and thus, decrement of the strength and the durability [8]. Similarly, Wamukonya and Jenkins [82], who focused on length expansion of binderless briquettes produced from wheat straw and/or sawdust over a week at 20°C and 50% relative humidity, concluded that the higher the length expansion, the lower the durability. On the other hand, equilibrium moisture contents of some commercially available biomass briquettes at relative humidity of 40–85% were observed by Singh [83], and it was concluded that storage of the briquettes at high humidity conditions (>70%) would not cause any problem.

4.5 Some of the Briquetting Studies in Literature

4.5.1 Studies carried out in Turkey

Kural [84] produced hot and cold briquettes from Sivas–Kangal lignite with and without using binder. Mechanical strength of the binderless briquettes was found to be proper by contrast with water resistance properties. However, improving water resistance properties of the briquettes was also reported to be possible by adding a binder material (i.e. sulfide liquor and latex).

Kural et al. [85] focused on using atactic polypropylene (a by-product of polypropylene plants) and its partially oxidized emulsions as a binder, and found that they have many advantages in addition to absence of disadvantages of other commercial binders (i.e. molasses, sulphide liquor, tar, bitumen, and clay).

Akgün et al. [86] investigated the hot and cold type briquetting of Konya–Ermenek lignite with or without using binder (i.e. atactic propylene, coal tar pitch, molasses, and sulphide liquor), and found that either hot and cold type binderless briquettes showed insufficient quality, whereas best binder was coal tar pitch between other examined binders.

Sağlam et al. [62] produced briquettes at 80°C under 100 MPa pressure from Yatağan, Soma and Tunçbilek lignite dusts by adding calcium sulphide liquor to promote decrease in environmental pollution owing to binding properties of Ca^{2+} ions to combustible sulphur.

Gürbüz–Beker and Küçükbayrak [87] studied the briquetting of Kemerburgaz–Istanbul lignite with or without using binder (e.g. molasses, and Şırnak asphaltite) at two different pressures (i.e. 150 and 200 MPa), and reported that mechanical strength and water resistance of the binderless briquettes were low. It was also stated that a briquetting pressure of 200 MPa and a binder ratio of 12% were optimum, and briquettes produced from lignite with a moisture content of 13% with the addition of asphaltite showed best strength properties, whereas strongest briquettes were obtained from lignite with a moisture content of 8% by adding molasses.

Özgen [88] produced briquettes under a pressure of 555 MPa from Afşin–Elbistan lignite by using binder materials such as sawdust, beer industry waste, paper mill waste, and sunflower residue. She found that briquettes produced with a moisture

content of 15% and a binder content of 20% had proper compressive and impact strengths in contrast to insufficient water resistance.

Gürtuna and Özhan [89] manufactured briquettes under 1500–2000 kg/cm² pressure from the mixture of Muğla–Yatağan lignite and Siberian coal with or without addition of additives (e.g. molasses, linobind, sawdust, and paper mill waste). Blending with Siberian coal that had lower sulfur content and higher calorific value was found to reduce emissions and to increase in calorific value, whilst molasses, sawdust, and paper mill waste were determined to increase compressive and impact strengths of the briquettes.

Yıldırım and Özbayoğlu [90] obtained humic acid (ammonium nitrohumate) with a nitrogen content of 10.75% from Elbistan lignite after the application of nitric acid oxidation followed by ammoniation, and used the humic acid as a binder to increase water resistance and durability of the briquettes from Tunçbilek lignite fines.

Gürbüz–Beker et al. [91] produced briquettes from the mixture of low–grade Afşin–Elbistan lignite and high quality Siberian bituminous coal with and without using a binder, and fixed the bituminous coal content at 50% in the case of binder (i.e. sunflower shell, sawdust, and molasses) addition. Mixing lignite with bituminous coal was determined to increase calorific value, reduce sulfur and ash contents, and decrease mechanical stability. They indicated that briquettes prepared from a mixture of lignite and bituminous coal by adding a binder material (e.g. sawdust and molasses) had proper mechanical properties. However, obtained briquettes did not show resistance to water longer than 20 min.

Demirbaş and Şahin [92] prepared briquettes from wheat straws that were preheated at 80°C, under a briquetting pressure of 300–800 MPa by using cold briquetting method, and obtained abrasive resistant biobriquettes that did not show resistance to water.

Demirbaş [93] briquetted tea wastes containing 15–18% moisture, under 300–800 MPa pressure for 5–30 min, and reported that compressive strength of the briquettes were 36.2–37.1 MPa.

Demirbaş [94] prepared cylindrical briquettes from charcoal of hazelnut shell by using pyrolytic oil or tar as binder, and reported that best briquettes were obtained at 400 K under 800 MPa pressure.

Gürbüz–Beker [95] produced biocoal briquettes under 550–800 MPa from a mixture of lignite (80–88%) and woody materials (12–20%, i.e. sunflower shell, sawdust, and paper mill wastes) by using molasses as a binder in the ratio of 8%. She reported that mechanical strength of the briquettes was proper and the briquettes can easily be burned.

Haykırı–Açma et al. [96] prepared briquettes from the mixture of a Turkish lignite and a Siberian bituminous coal with or without a binder (e.g. sunflower shell, sawdust, and molasses), and investigated combustion characteristics of the briquettes.

Hiçyılmaz and Altun [97] prepared briquettes from Tunçbilek lignite with the addition of binders (i.e. molasses, carboxyl methylcellulose, sulfide liquor, corn starch, crude oil, lime, and sodium silicate) in the ratio of 10%. They found that activation energy and the residue at the end of the combustion decreased with the use of molasses and carboxyl methylcellulose, whereas calorific value increased with the use of sulfide liquor, corn starch, and crude oil. It was also stated that lime and sodium silicate were the most disadvantageous binders because of causing increase in activation energy and the residue at the end of the combustion in addition to decrease in calorific value.

Karaosmanoğlu [30] produced cold binderless biobriquettes at 150 MPa from extracted rapeseed cake with a moisture content of 10.1%, and reported the suitability of the briquettes to be used as fuel substitute.

Yaman et al. [4] produced cold briquettes from olive refuse and paper mill waste under 150–250 MPa pressure, and determined that strong and durable briquettes can be obtained either from paper mill waste alone or its mixture with olive refuse. They also reported that briquettes from the 1:1 mixture of olive refuse and paper mill waste under 200 MPa pressure had a Shatter Index of 4813, a compressive strength of 319 kg/cm², and a water resistance of 27 min.

Altun et al. [98] prepared coal briquettes from Tunçbilek lignite by using binders such as molasses, carboxyl methylcellulose, sulfide liquor, heavy crude oil, sodium silicate, corn starch, lime, peridur, bentonite, cement, and polyvinyl acetate. They determined that molasses and carboxyl methylcellulose decreased the residue at the

end of combustion, whereas sulfide liquor, heavy crude oil, and corn starch increased the calorific value.

Yaman et al. [2] briquetted Kütahya–Seyitömer lignite under 50–250 MPa pressure by blending with biomass materials (i.e. molasses, pine cone, olive refuse, sawdust, paper mill waste, and cotton refuse), and found that paper mill waste was a good binder owing to its positive effects on compressive strength, abrasive resistance and water resistance of the briquettes. It was also observed that blending with sawdust enhanced compressive strength of the briquettes, whilst addition of olive refuse, cotton refuse or pine cone increased water resistance of the briquettes.

Yıldırım and Özbayoğlu [99] produced durable and water-resistant coal briquettes at 165°C under a briquetting pressure of 126 MPa for 1 h with the use of coal-derived humic acid extracted from Afşin–Elbistan lignite as a binder in the ratio of 5%, and reported that the radial compressive strength and the abrasive resistance were determined as 80 kg/briquette and 87.03%, respectively.

Altun et al. [23] investigated the influences of binder type (i.e. organic (molasses, sulfide liquor, carboxyl methyl cellulose, Peridur XC3, and Peridur C10), or inorganic (cement and bentonite) agents), binder content and water addition on combustion efficiency and thermal behaviors of fuel in terms of the changes in the amounts of evolved CO and CO₂, and consumed O₂ gases as a function of time and temperature, the O₂ peak times and temperatures, and the remaining residue at the end of each run. They reported increase in efficiency, effectiveness, and extent of combustion and improvement in thermal quality of the briquettes with the addition of organic binders (except sulfide liquor). It was also stated that carboxyl methyl cellulose was the best binder by virtue of highest O₂ consumption, highest peak temperature, lowest peak time, and lowest residue amount.

Altun et al. [100] also studied the effects of binder type, binder content and water addition on reaction kinetics (e.g. activation energy and Arrhenius constant), and concluded that adding organic binders, increasing binder addition ratio, or decreasing water addition ratio increased the liability of the briquettes to ignite and combust due to decrease in activation energy, whereas inorganic binder addition showed opposite effects. Besides, it was reported that carboxyl methyl cellulose was the best binder due to lowest activation energy.

Demirbaş et al. [50] investigated briquetting properties (i.e. heating value, compressive strength, abrasive resistance, water resistance, and combustion behaviors) of the briquettes obtained from pulping reject and spruce wood sawdust. They found that strongest briquettes were produced at 350 MPa from spruce wood sawdust with a moisture content of 15%, and that compressive strength and shatter index of the briquettes were 49.5 MPa and 20500, respectively.

Yıldırım and Özbayoğlu [101] briquetted Tunçbilek lignite fines by using ammonium nitrohumate, which is a low calorific valued, young lignite-derived, humic acid salt solution, as a binder, and reported the manufacturing of the durable briquettes with a binder content of 7% and a moisture content of 10.5%.

Dahiloğlu [102] produced briquettes from the mixture of Afşin–Elbistan lignite and biomass materials (i.e. hazelnut shell, sunflower husk, rice husk, and prina) by using a binder (e.g. molasses, sulfide liquor, or linobind). She reported increase in water resistance and decrease in compressive and impact strengths of the briquettes with the increase in binder content, and determined the optimum parameters such as briquetting pressure and biomass content.

Oyacı and Kaner [103] prepared briquettes under 833 MPa pressure from the mixture of Soma–Deniş lignite and biomass materials (10%, i.e. sesame husk, potato peel, cacao husk, and black cumin residue) with or without a binder material (e.g. molasses, and linobind (modified starch)). Burnout temperature, maximum combustion rate, and maximum combustion rate temperature of the briquettes were found to be 24–32 min, 3–14 mg/min, and 146–200°C, respectively. Compressive strength of the briquettes produced with the addition of biomass and/or binder were determined to be proper according to Turkish National Standards, whilst impact strength and water resistance of these briquettes did not meet with the standards.

4.5.2 Studies carried out in the World

4.5.2.1 Germany

Köser et al. [104] reported that water hyacinth containing high moisture content, which has no economical value, can easily be briquetted without a binder after an open–air drying process followed by a combination of disintegration and screening processes to reduce ash content of the plant to 12%.

Naundorf [105] claimed that water resistance of the briquettes can be improved with some precautions such as mixing raw coal with coke dust and/or fibrous substances, rewetting over dried coal in an intensive mixer, climatic pretreatment at elevated temperature ($\sim 80^{\circ}\text{C}$) and high air humidity (80%), and pressing of pretreated coal. Naundorf [106] also stated that quality of soft and hard brown coals with a saturation water content above 26% increased owing to reactivation of binding forces by crushing under hydrothermal conditions in equipments such as vibrating ball mills and twin screw crushers.

4.5.2.2 Japan

Shimamura et al. [107] produced high quality briquettes from low rank coal by using a method that contains wet milling, refining with hot water at $\geq 270^{\circ}\text{C}$ for ≥ 5 min, drying refined coal, and pressing with charcoal powder and a binder under ≥ 2 ton/cm², respectively.

Kato and Komaki [108] produced briquettes from the mixture of powdered coal (70–100% of particle size of < 3 mm) and ironmaking dust (1–10%, i.e. blast–furnace dust, steelmaking dust, and sintered dust) by adding a binder into the mixture, heating and molded, respectively.

Kim et al. [28] manufactured biocoal briquettes by using pulp black liquor (a by–product of pulp production industry) as a binder and reported reduction in SO₂ emissions related to desulphurization characteristics of pulp black liquor as well as increase in mechanical strength and improvement in combustion properties.

Suzuki et al. [109] produced briquettes by mixing coal powder with plastic powder or shredder dust waste that have superior flammability and higher calorific value than coal, and dewatered sludge powder that have less flammability and lower calorific value than coal; grinding the mixture of coal (66%), shredder dust (2%), and dewatered sludge powder (32%); extruding with a binder, and drying, respectively. They determined the calorific value of these briquettes as 5150 cal/g.

Shimazaki et al. [110] obtained briquettes with higher heating value and less manufacturing cost from coal powder (grain size of ≤ 5 mm for $\geq 50\%$; moisture content of $\geq 15\%$) by adding starch binder (1–10%), extruding the mixture, coating with heavy oils (0.1–5%) on surface, and extruding in a double roll molding machine, respectively.

Shimizu [111] manufactured briquette rods that were suitable for picnic or camping by consolidating low rank coal powder with sawdust and sugar, and capping the ends of the rods for integrity.

4.5.2.3 Malaysia

Chin Chin and Siddiqui [69] briquetted biomass materials (i.e. sawdust, rice husks, peanut shells, coconut fibers, and palm fruit fibers) at moderate pressures (5–7 MPa), and stated that optimum conditions varied due to biomass type. Also, sawdust was reported to be the best due to its storage behaviors and lack of deterioration.

Husain et al. [112] focused on briquetting of palm oil production wastes (i.e. fiber, shell, and empty fruit bunches) under moderate pressure (5–13.5 MPa) by using a hydraulic press, and produced briquettes with a bulk density of 1100–1200 kg/m³, a calorific value of 16.4 MJ/kg, an ash content of 6%, an equilibrium moisture content of about 12%, and proper mechanical strength and water resistance values.

4.5.2.4 People's Republic of China

Zhang [113] produced briquettes by mixing raw coal with solid binders of quick lime (3–5%) and bentonite (5–8%), and a liquid binder (~10%), which was obtained from industrial gelatin and acetic acid with the gelatin:acetic acid:water ratio of 1:(3–5):(150–200) or diluted sulphite liquor (a by-product of paper mill waste) with the sulphite liquor:water ratio of 1:(3–5), followed by crushing and shaping 2 hours later, respectively.

Zhang et al. [114] reported a method for briquette manufacturing, in which crushed coals with a particle size of 0–20 mm were mixed with water in the coal:water ratio of (4–8):1, the coal–water blend with a viscosity value above 1 was shaped and cutted, respectively, by using a system containing three conveyors, two crushers, two pusher type mixers, one screw pusher forming machine, a pallet, a cut off machine, and an auxiliary power equipment.

Zhenhui [115] obtained environmental friendly coal briquettes with the addition of a combustion supporting binding agent that composed of danty (weathered coal), lignite, gang (coal mining residues), hydroxides (NaOH or KOH), and carbonates (K₂CONa₂CO₃) into coal.

Wang [116] briquetted powdered coals at 50–80°C under high pressure for 24–48 h by adding a liquid additive in the ratio of 1–20%, which was prepared by diluting the blend of elm dust (3–10%), calcium oxide (10–20%), hydrochloric acid (4–16%), coke dust (10–20%), charcoal dust (5–10%), vermiculite (2–8%), antimony ore (2–6%), silica (2–6%), and wood dust or stalk (10–40%) with clean water for 3–4 times, to improve combustion properties.

Zhang et al. [117] investigated the utilization of rice straw-based binders in coal briquettes from Pingzhuang lignites, and prepared briquettes under 294 MPa pressure with the addition of binder materials, which were produced by treating of rice straw with sodium hydroxide, lime, or sulfuric acid. It was reported that solid and liquor components of rice straw treated with sodium hydroxide, and solid component of rice straw treated with lime could be used as a binder, whilst rice straw treated with sulfuric acid did not show binding ability. They also indicated that addition of bentonite, coal tar, and/or polypropylene amide into rice straw-based binder would gain water proof property to the briquettes.

Chen et al. [118] produced cold briquettes from bituminous coal with high or low volatile matter and anthracite with the use of binders, and investigated the ignition mechanisms of the briquettes. They found that ignition mechanism was heterogeneous when the furnace temperature was lower than 600°C, whereas ignition mechanisms were homogenous for bituminous coal with high volatile matter and heterogeneous for bituminous coal with low volatile matter and anthracite when the furnace temperature was higher.

Hao et al. [119] obtained waterproof honeycomb shaped briquettes from anthracite dust (40–80%), silt coal (10–40%), gangue (10–30%), clay (4–20%), sulfur fixing agent (4–15%), catalyst (0.1–3.0%), combustion improver (0.1–1.0%) such as nitrate, MnO_2 , KMnO_4 or NaCl , and auxiliary agent (0.1–3.0%) such as MgO , Al_2O_3 , or magnesia mineral. Ca compound (i.e. lime or carbide slags) was used as a sulfur fixing agent, and the molecular ratio of Ca in the agent to sulfur in the coal was selected to be (1.5–3.5):1.

Zhang [120] produced honeycomb shaped briquettes by pressing an ignition layer that contains a blend of coal (800–1200), KMnO_4 (0.1–2.0), CaO (20–40), metaformaldehyde (0.5–2.0), polyethylene glycol (0.3–3.0), vegetable stalk (200–

400), and yellow earth (400–600) onto a combustion layer, which composed of a mixture of coal (800–1200), NaNO_3 (0.5–2.0), KMnO_4 (0.1–2.0), CaO (20–40), NaCl (0.5–3.0), metaformaldehyde (0.5–2.0), vegetable stalk (200–400), and yellow earth (400–600).

Ma et al. [121] produced briquettes from blends of coal and biomass at an industrial plot scale, and reported that lower reasonable limit of biomass content was 15%, and that a briquetting pressure above 120 MPa had detrimental effects on the briquette quality. It was also indicated that 15 kWh of power consumed per ton briquette, which was less than 1/3–1/5 of that in traditional process, whereas total processing cost was US\$2.5 per ton briquette including capital investment and operating cost. They also determined that 50–60% of the sulfur content was captured with the addition of a proper sulfur retention reagent.

Qu and Zhou [122] used an additive that contains CaO (10–30), KMnO_4 (3–15), MnO_2 (3–15), MgO (1–5), KCl (1–5), and $\text{Ba}(\text{NO}_3)_2$ (1–5) for coal briquettes, and determined increase in heating value and reduction in noxious emissions.

Liu [123] produced briquettes with high combustion efficiency and reduced noxious emissions by pressing a mixture of coal powder, clay (3.5%), quartz sand (3.5%), sawdust (10%), stalk powder (10%), and water (45%), drying at 100°C, calcining at 1300°C for 30 min, respectively.

Zhou and Zhou [124] obtained briquettes from a mixture of coal dust (84–92%) and silicate cement (8–16%) by mixing this mixture with a certain amount of water, compressing, drying, and calcining, respectively.

4.5.2.5 Poland

Wawerla et al. [125] manufactured briquettes from dried coals (i.e. 4–6%) by adding starch (optionally modified starch) before and/or after dried to hygroscopic moisture content, and mixing the charge, followed by addition of urea–formaldehyde resin of <2%, hydrophobization of briquettes with the addition of polyvinyl acetate, and hardening at 95–110°C, respectively, and reported that these briquettes released less smoke during combustion, and showed more resistance to weathering.

Zakrzewski et al. [126] produced briquettes with high strength, mould resistance, and water resistance from coal fines (<6 mm) by mixing with 4–10% binder (i.e. a

mixture of starch and molasses in the ratio of (1–3):(1–3)) and 0.1–0.5% hardener (e.g. 86% phosphoric acid and/or aluminium–potassium sulfate), conventional briquetting, drying at $\leq 95^{\circ}\text{C}$ to achieve a moisture content of $< 2\%$, and hardening at $120\text{--}200^{\circ}\text{C}$ for 0.5–1.5 h.

4.5.2.6 Russia

Lury and Terentiev [127] produced briquettes from a mixture of powdered solid fuel and water soluble organic binder (i.e. 30–40% aqueous solution of sodium salt of methylene naphthalene sulfonic acid or lignosulfonate) by enclosing the mixture with a moisture content below 9% in combustible casings, compacting and hardening.

There were also some studies reported to be on production of briquettes from hydrolytic lignin (a by-product of hydrolysis industry) by Bridaev [128], from powdered coal and wood wastes by Gomzar and Nezametdinov [129], from brown coal, lignin, or sawdust by Pushkanov et al. [130], from brown coal and petroleum asphaltites by Pushkanov et al. [131], from coal, lignite, peat and cellulose nitrate by Kostochko et al. [132] in Russia.

4.5.2.7 South Africa

Mangena and du Cann [133] prepared binderless briquettes from South African prime coking and blend coking coals, and from inertinite-rich bituminous coals. They reported that the most successful briquettes were obtained from fresh, vitrinite-rich coking and blending coking coals by virtue of deformation and subsequent consolidation of vitrinite macerals, whereas satisfactory briquettes were produced from fresh, inertinite-rich bituminous coals.

Motaung et al. [134] prepared pillow-shaped, water-resistant, binderless briquettes under 17 MPa pressure by using flotation concentrates and flotation feeds of six different bituminous coals from the Witbank Coalfield. It was determined that briquettes produced from flotation concentrates showed more water resistance than that of flotation feed, which may be associated with the combination effect of fineness of the coal particles, presence of the reactive macerals (particularly vitrinite), presence of the flotation reagents (especially the paraffin-based collector), and lower contents of ash and kaolinite.

4.5.2.8 Thailand

Chaiklangmuang et al. [135] prepared cylindrical biocoal briquettes by applying a pre-treatment with 3% and 7–13% sodium hydroxide solutions for rice husk and sawdust biomasses, respectively, at 80°C for 1.5–4.5 h, and mixing lignite with biomass in equal amounts.

Wilaipon [31] prepared biocoal briquettes by applying a pre-treatment with sodium hydroxide to maize cob that has a calorific value of 14.2 MJ/kg, mixing coal fine with pre-treated maize cob in the coal:maize ratio of 1:(2–3), and briquetting the mixture under 4–8 MPa.

4.5.2.9 Other Countries

Ellison and Stanmore [136] produced binderless vacuum-dried Victorian brown coal briquettes with a diameter of 29.5 mm at elevated temperatures (above 130°C) and conventional pressures in the absence of oxygen, and reported that the briquettes have comparable compressive strengths to some long chain polymers.

Richards [137] reported that peat from Ohinewai deposits of the Waikato River Valley region of New Zealand can be successfully briquetted without binder, and can be used as a binder in the briquetting process of surplus sub-bituminous coal fines from the nearby Waikato coalfield. It was also stated that extremely high quality briquettes were produced from peat and peat-coal blends containing up to about 50% coal either in the laboratory scale studies and pilot extrusion studies, which were carried out in a wood waste briquetting press.

Rupp-Dahlem [138] informed the development of a proprietary starch system by Roquette Company for briquetting of coal fines. It was reported to be environmental friendly alternative to traditional binders (e.g. pitch, bitumen, and lignosulfonates) owing to lower black smoke, zero added sulfur, and superior water resistance. Some technical and economical advantages in comparison to other standard binders and ammonium salts (i.e. sulfate, phosphate, and nitrate) were also stated when used with ammonium chloride under defined conditions.

Musat et al. [139] produced cylindrical briquettes from a blend of agricultural wastes (especially straw, 10–15%), dimeterephthalate manufacture waste (35–45%), and

coke/coal dust (40–50%) after homogenization, and pressing at 100–150 N/cm², respectively.

Kim et al. [140] reported a briquette producing method, in which pressed upper layer that contains barium nitrate (12%), sodium nitrate (2%), mugwort (0.1%), and powdered charcoal (25%) coated on pressed lower layer that composed of barium nitrate (8%), sodium nitrate (1%), mugwort (0.1%), powdered charcoal (30%), and steam coal (15%) with a binder solution prepared with starch (6.4%), serpentine (0.3%), mugwort (0.1%), and water (30g), and briquettes were heated with steam, and were coated with a solution of nitrocellulose (30–40%) and acetone (60–70%), and optionally with an inorganic dye.

Tai and Sharon [141] obtained briquettes from charcoal (10–65), anthracite (35–90), and a starch binder by incorporating with an accelerant (e.g. a mixture of Na(NO₃)₂ and Ba(NO₃)₂) on the top and other ignition surfaces for simplifying ignition.

Debdoubi et al. [142] produced briquettes from esparto, which is the most abundant biomass of Morocco and does not require any predrying procedure owing to its low water content (5%), by applying partial pyrolysis at 160–400°C to increase calorific value, to reduce volatile matter content, and to improve mechanical properties, followed by briquetting at elevated pressure, and observed increase in water resistance and decrease in impact strength with the pyrolysis process. They also stated that combustion profile of pre-pyrolyzed esparto briquettes was very similar to that of coal.

Jha et al. [54] produced square briquettes from chopped cotton stalks by using a vertical compaction machine, and proposed a second order polynomial in order to correlate physical characteristics (i.e. bulk density, resiliency, hardness, and compression ratio) with moisture content and briquetting pressure.

Taulbee et al. [22] evaluated effects of 50 potential binders on briquettes produced from bituminous coal by adding oak sawdust (10%) and water (5%), compressing under 28 MPa pressure for 3 s, and curing at 22°C under 80% relative humidity. They reported that guar gum and wheat starch were the most suitable binders for pulverized coal market, whilst lignosulfonate was targeted for the stoker market.

5. EXPERIMENTAL STUDIES

5.1 Samples

5.1.1 Coal sample

Coal sample used in the experimental studies was obtained from Çorum–Bayat lignite deposit of Turkey. The coal sample was first dried under ambient conditions to increase their grindability, and then ground to obtain a sample reduced to 250 μm tosize. After that, characterization analyses (see **Ch. 5.3**) and briquetting procedures (see **Ch. 5.4**) were applied. Characteristic properties of the coal sample are summarized in **Tables 5.1–5.3**.

5.1.2 Biomass samples

Biomass samples used in the experimental studies were hazelnut refuse and thick syrup residuum wastes (grape, locust, or mulberry). Hazelnut refuse consisted of the remaining plants after the fruit parts were removed from the hazelnut during harvesting process, whilst TSR wastes (see **Figure 5.1**) were the industrial residues of Dutpinar Food Trade Industry Ltd., Co.



Figure 5.1 : Thick syrup residuum wastes (a. grape TSR waste, b. locust TSR waste, c. mulberry TSR waste).

Table 5.1 : Results of the elemental analyses of the samples.

Samples		Elemental Analyses (% ash free basis)				
		C	H	O	N	S
Coal sample	Çorum–Bayat lignite	6.12	74.93	13.52	1.94	3.50
	Hazelnut refuse	5.53	50.11	43.25	1.00	0.10
Biomass samples	Grape TSR waste	5.96	51.70	40.16	2.08	0.10
	Locust TSR waste	5.43	57.56	35.61	1.33	0.07
	Mulberry TSR waste	7.45	57.84	31.61	2.98	0.13
Binder	Plant root	6.77	42.69	48.41	1.93	0.21

Table 5.2 : Results of the proximate analyses and the calorific value measurements of the samples.

Samples		Proximate Analyses (%)				Calorific Value (MJ/kg)	
		Moisture	Volatile Matter	Fixed Carbon	Ash	Low	Gross
Coal sample	Çorum–Bayat lignite	7.50	35.00	28.25	29.25	19.23	20.51
	Hazelnut refuse	4.50	80.50	11.25	3.75	15.58	17.01
Biomass samples	Grape TSR waste	5.75	75.00	12.00	7.25	16.26	17.72
	Locust TSR waste	5.75	69.25	18.75	6.25	17.05	18.51
	Mulberry TSR waste	5.00	70.00	6.25	18.75	17.18	18.63
Binder	Plant root	9.25	79.00	3.00	8.75	14.00	15.55

Table 5.3 : Results of the combustion analyses of the samples.

Samples		Maximum Burning		Burning Time (min)
		Temperature (°C)	Rate (mg/min)	
Coal sample	Çorum–Bayat lignite	285.0	2.50	45.6
	Hazelnut refuse	160.0	21.75	24.0
Biomass samples	Grape TSR waste	176.0	16.25	26.0
	Locust TSR waste	173.5	12.50	32.8
	Mulberry TSR waste	160.0	13.75	28.0
Binder	Plant root	155.5	17.50	23.6

The biomass samples were first dried at 105°C, and then ground to obtain samples passing through a sieve with a screen size of 250 µm. After that, characterization analyses (see **Ch. 5.3**) and briquetting procedures (see **Ch. 5.4**) were conducted. Characteristic properties of the biomass samples are given in **Tables 5.1–5.3**.

5.1.3 Binders

Binders used in the experimental studies included molasses and linobind. Molasses, which was a by-product of sugar extracting process from the sugar beet, was a thick, uncrystallizable, and dark brown syrup, whereas linobind was a starch-based solution. On the other hand, the plant root solution was a 0.1 g/mL water solution of a silvatic plant root. The same procedures with the biomass samples were performed for the plant root before used for the solution preparation. Characteristic properties of the plant root are shown in **Tables 5.1–5.3**.

5.2 Equipments

5.2.1 Elemental analyses equipment

Elemental analyses were achieved by using a Leco TruSpec® CHN model instrument with a Leco TruSpec® S module (see **Figure 5.2**).



Figure 5.2 : A Leco TruSpec® CHN model instrument with a Leco TruSpec® S module for elemental analyses.

5.2.2 Calorific value analyses equipment

Calorific value analyses were carried out by using a IKA C2000 Basic Calorimeter with a stainless steel calorimeter bomb (see **Figure 5.3**).



Figure 5.3 : A IKA C2000 Basic Calorimeter with a stainless steel calorimeter bomb.

5.2.3 Thermogravimetric analyses equipment

Thermogravimetric analyses were performed to achieve the proximate analyses and the combustion properties by using a Shimadzu TG41 Thermal Analyzer (see **Figure 5.4**) with a maximum operation temperature of 1500°C. The analyzer consists of a cylindrical alumina sample container with a diameter of 10 mm and a height of 14 mm, and a thermocouple of Pt- Rh alloy.



Figure 5.4 : A Shimadzu TG41 Thermal Analyzer.

5.2.4 Briquetting equipments

Briquetting experiments were carried out by using a briquetting die and a briquetting press, which were produced specially by Erikman Brothers Machine and Electrical Industry Company. The briquetting press (see **Figure 5.5**) was a calibrated, laboratory-scale hydraulic press with a maximum pressurizing capacity of 3470 MPa, whereas the briquetting die was a cylindrical, hardened steel mold with an inner diameter of 30 mm.

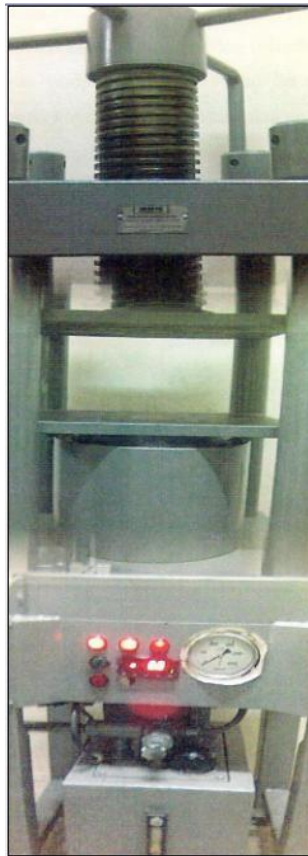


Figure 5.5 : The laboratory-scale hydraulic briquetting press.

5.3 Characterization of the Coal and the Biomass Samples

In order to obtain sample characteristics, the elemental analyses, the calorific value analyses, the proximate analyses, and the combustion analyses were performed. All of the characterization analyses were achieved in accordance with ASTM Standards [143–146].

5.3.1 The proximate analyses

The proximate analyses were carried out in a thermal analyzer by using 40 mg of the samples with a particle size smaller than 250 μm . Firstly, temperatures of the samples were increased to 105°C with a heating rate of 10°C/min, and kept constant at this temperature for 10 min under a nitrogen stream of 40 mL/min in order to remove moisture content. Then, temperatures of the samples were raised to 900°C with a heating rate of 40°C/min, and kept constant at this temperature for 7 min under a nitrogen stream of 40 mL/min in order to eliminate volatile matter content. Finally, temperatures of the samples were decreased to 755°C for coal and to 600°C for biomass with a cooling rate of 20°C/min under a nitrogen stream of 40 mL/min, and kept constant at this temperature in the presence of a dry air stream of 40 mL/min until the sample weights became constant. All of the proximate analyses were achieved with a chart speed of 1.25 mm/min.

5.3.2 The combustion analyses

The combustion analyses were performed in a thermal analyzer by using 40 mg of coal or biomass samples with a particle size smaller than 250 μm . Firstly, temperatures of the samples were increased to 900°C with a heating rate of 40°C/min in the presence of a dry air stream of 40 mL/min, and then, kept constant at this temperature until the sample weights became constant. All of the combustion analyses were achieved with a chart speed of 2.5 mm/min, and the DTG diagrams shown in **Figure 5.6** were obtained. These DTG diagrams were used for the determination of maximum burning rate, maximum burning rate temperature, and burning time (see **Table 5.3**).

5.4 Briquetting Procedure

Firstly, a series of experiments was conducted to determine the effects of different briquetting pressures on the quality of the briquettes produced from coal or biomass samples. For this purpose, the lignite sample and the biomass samples were briquetted separately under briquetting pressures of 350, 700 and 1000 MPa.

After that, the effects of different briquetting pressures on the quality of the biocoal briquettes manufactured from lignite–hazelnut refuse blends were

investigated. To achieve this, the lignite–hazelnut refuse blends were prepared to contain 10, 15, and 20 wt% hazelnut refuse, and were briquetted by applying briquetting pressures of 350, 700 and 1000 MPa.

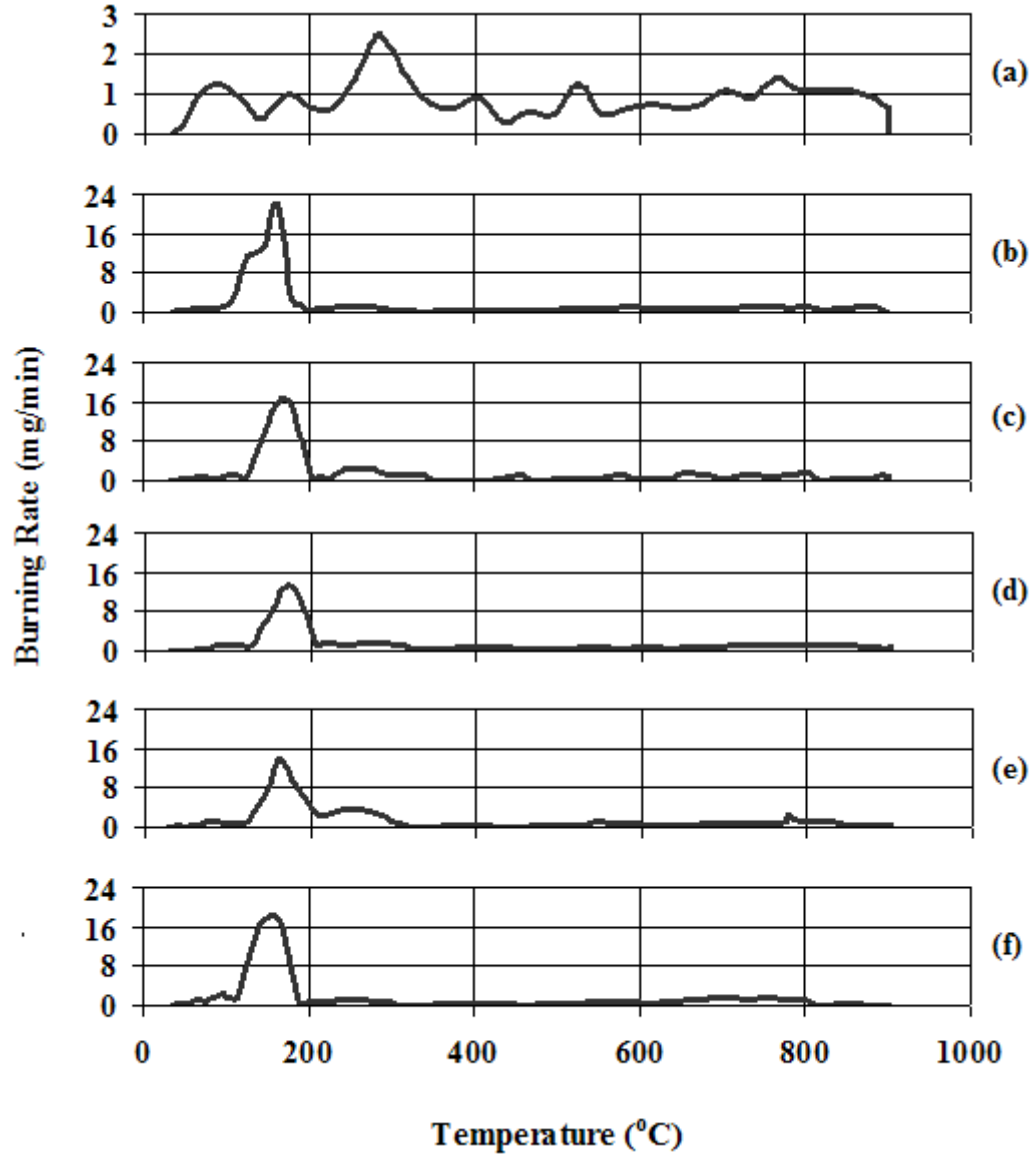


Figure 5.6 : DTG diagram of the samples (a. Çorum–Bayat lignite, b. hazelnut refuse, c. grape TSR waste, d. locust TSR waste, and e. mulberry TSR waste, f. plant root).

Another series of experiments was carried out to find the effects of different biomass types and contents on the quality of the binderless biocoal briquettes prepared under a briquetting pressure of 700 MPa. These biocoal briquettes were produced from lignite–biomass blends containing 0, 5, and 10 wt% TSR waste (e.g. grape, locust, or mulberry), or 0, 10, 15, and 20 wt% hazelnut refuse as biomass materials.

Moreover, a series of experiments was achieved for studying the effects of different briquetting times on the impact strength of the binderless biocoal briquettes. For this reason, the lignite–biomass blends containing 10 wt% TSR waste or 20 wt% hazelnut refuse were produced by applying a briquetting pressure of 700 MPa.

Furthermore, a series of experiments was performed to determine the effects of different binder types on the quality of the biocoal briquettes. Thus, the lignite–biomass blends having 90:10 (wt%) coal:TSR waste ratio or 80:20 (wt%) coal:hazelnut refuse ratio were briquetted with the addition of three different binders under a briquetting pressure of 700 MPa. Binder contents of these biocoal briquettes were set as 10, 4, and 10 wt% for molasses, linobind, and plant root solution, respectively.

For each experiment, 10 g of samples were filled into the briquetting die, and briquetted under ambient conditions by applying various pressures with the briquetting press. Obtained briquettes (see **Figure 5.7**) were cylindrical in shape with a cross sectional area of 7.07 cm^2 , and were stored in zipped plastic bags under ambient conditions for 7 days before testing their quality parameters to stabilize inner tensions affecting the microstructure and porosity of the briquettes.



Figure 5.7 : Examples of the briquettes manufactured from the biomass or the coal samples.

5.5 Testing Methods for Quality Parameters of the Briquettes

Compressive strength, impact strength, and water resistance tests were performed to study quality parameters of the briquettes. Two briquettes prepared for each set of experimental conditions were used for testing, and the arithmetic averages of the measurements were calculated to examine the quality of the briquettes. All of the tests were achieved in accordance with TS 12055 [147].

5.5.1 Compressive strength test

Compressive strength tests of the briquettes were conducted at an Instron table model 1195 testing machine by placing a briquette between two flat and parallel plates that have greater facial areas than the area of the briquette, and applying an increasing load at a constant rate until the briquette was cracked or broken. The load at fracture was reported as compressive strength.

5.5.2 Impact strength test

Impact strength tests of the briquettes were carried out by subjecting them to six repeated drops from 1.20 m height onto a steel plate, and passing all the pieces through a series of sieves with screen sizes of 30, 25, 20, 16, 10, and 5 mm after the sixth drop. The impact strength values were calculated by Eqs. (5.1) and (5.2), in which m_i and l_i refer to total mass and average length of the pieces above the i -numbered sieve, whereas m and l represent weight and diameter of the intact briquettes.

$$l_{ave.} = \sum_{i=1}^5 \frac{m_i \times l_i}{m} \quad (5.1)$$

$$Impact\ Strength\ (\%) = \frac{l_{ave.}}{l} \times 100 \quad (5.2)$$

5.5.3 Water resistance test

Water resistance tests of the briquettes were performed by immersing them into a container filled with water at room temperature. The time required for the onset of dispersion in water was taken as water resistance.

6. RESULTS and DISCUSSION

6.1 Effect of Briquetting Pressure on Quality of the Briquettes

The effect of briquetting pressure on the quality of the briquettes produced from lignite or biomass samples were determined in terms of compressive strength, impact strength, and water resistance. These experiments were conducted without using any additive or binder material.

6.1.1 Effect of briquetting pressure on compressive strength

In order to determine the effect of briquetting pressure on compressive strength of the briquettes, lignite and biomass samples were briquetted separately with no additives by applying three different briquetting pressures. Compressive strength values of these briquettes are given in **Table 6.1**.

Table 6.1 : Effect of briquetting pressure on compressive strength of the briquettes.

Briquetting Pressure (MPa)	Compressive Strength (kg/cm ²)				
	Çorum – Bayat Lignite	Hazelnut Refuse	TSR Waste		
			Grape	Locust	Mulberry
350	96.06	49.73	232.51	17.61	63.03
700	124.00	561.53	508.23	89.76	77.38
1000	165.38	838.61	890.21	91.39	90.82

In the light of these experimental findings, it can be calculated that increasing briquetting pressure from 350 MPa to 700 MPa improved compressive strength of the Çorum–Bayat lignite, the hazelnut refuse, the grape TSR waste, the locust TSR waste, and the mulberry TSR waste containing briquettes 29, 1029, 119, 408, and 23%, respectively, whilst increasing briquetting pressure from 700 MPa to 1000 MPa raised compressive strength of these briquettes 33, 49, 75, 2, and 17%, respectively. Therefore, it can be reported that compressive strength of the formed briquettes increased with the increase in briquetting pressure. However, increasing the briquetting pressure from 700 MPa to 1000 MPa was not as effective as increasing it from 350 MPa to 700 MPa. Ndiema et al. [27] also indicated that there is a maximum briquetting pressure beyond which no significant gain cohesion (bonding) of the

briquette can be achieved. Thus, 700 MPa can be chosen as the optimum briquetting pressure.

Moreover, the lignite, the hazelnut refuse, and the grape TSR waste containing briquettes prepared under briquetting pressures of 700 and 1000 MPa were met with the requirements of TS 12055 in terms of compressive strength, since minimum acceptable values are 100 kg/cm² for class II briquettes and 130 kg/cm² for class I briquettes. However, none of the briquettes manufactured from locust or mulberry TSR waste samples had sufficient compressive strength.

On the other hand, the hazelnut refuse and the grape TSR waste containing briquettes produced under briquetting pressures of 700 and 1000 MPa showed similar compressive strength characteristics with each other, which were better compared to that of the lignite briquettes. Hence, addition of hazelnut refuse or grape TSR waste into the lignite briquettes may enhance compressive strength of the formed briquettes.

6.1.2 Effect of briquetting pressure on impact strength

In order to determine the effect of briquetting pressure on impact strength of the briquettes, lignite and biomass samples were briquetted separately without using additives under three different briquetting pressures. Impact strength values of these briquettes are shown in **Table 6.2**.

Table 6.2 : Effect of briquetting pressure on impact strength of the briquettes.

Briquetting Pressure (MPa)	Impact Strength (%)				
	Çorum – Bayat Lignite	Hazelnut Refuse	TSR Waste		
			Grape	Locust	Mulberry
350	11.78	7.49	75.63	0	99.85
700	26.65	98.36	97.39	0	99.26
1000	33.98	99.30	97.69	0	99.84

According to these experimental findings, it can be reported that increasing briquetting pressure from 350 MPa to 700 MPa enhanced impact strength of the Çorum–Bayat lignite, the hazelnut refuse, and the grape TSR waste containing briquettes 126, 1213, and 29%, respectively, whilst increasing briquetting pressure from 700 MPa to 1000 MPa raised impact strength of these briquettes 27, 1, and 0.3%, respectively. Therefore, it can be reported that impact strength of the

biobriquettes prepared from hazelnut refuse or grape TSR waste increased with the increase in briquetting pressure until a threshold value (700 MPa), above which no significant effects were seen, whereas impact strength of the lignite briquettes were more affected from the increase in briquetting pressure from 700 MPa to 1000 MPa. Similarly, Chin Chin and Siddiqui [69] found that quality of the rice husk biobriquettes improved as the briquetting pressure increased. Li and Liu [5] studied the briquetting behaviours of oak sawdust, oak mulch, oak bark, oak chips, pine sawdust, cottonwood sawdust, and cottonwood mulch applying briquetting pressures between 34–138 MPa. They found that increasing pressure increased the abrasive resistance and the hardness of logs made from these biomass materials.

On the other hand, impact strength of the locust TSR waste and the mulberry TSR waste containing biobriquettes did not change with the briquetting pressure.

Moreover, biobriquettes manufactured under briquetting pressures of 700 and 1000 MPa from hazelnut refuse, grape TSR waste or mulberry TSR waste were met with the requirements for class I briquettes in terms of impact strength, since minimum acceptable value is 90% according to TS 12055. However, none of the briquettes produced from lignite or locust TSR waste samples had sufficient impact strength. Thus, adding hazelnut refuse, grape TSR waste, or mulberry TSR waste into the lignite briquettes may improve impact strength of the formed briquettes.

6.1.3 Effect of briquetting pressure on water resistance

In order to determine the effect of briquetting pressure on water resistance of the briquettes, lignite and biomass samples were briquetted separately without any additives by applying three different briquetting pressures. Water resistance values of these briquettes are given in **Table 6.3**.

Table 6.3 : Effect of briquetting pressure on water resistance of the briquettes.

Briquetting Pressure (MPa)	Water Resistance (s)				
	Çorum – Bayat Lignite	Hazelnut Refuse	TSR Waste		
			Grape	Locust	Mulberry
350	57.50	6.50	30.53	11.38	2666.69
700	47.67	7.40	33.20	11.95	2940.25
1000	64.76	14.22	46.33	16.66	3116.54

Experimental findings showed that increasing briquetting pressure from 350 MPa to 700 MPa increased water resistance of the hazelnut refuse, the grape TSR waste, the locust TSR waste, and the mulberry TSR waste containing biobriquettes 14, 9, 5, and 10%, respectively, whilst increasing briquetting pressure from 700 MPa to 1000 MPa raised water resistance of these biobriquettes 92, 40, 39, and 6%, respectively. Therefore, it can be reported that water resistance of the formed biobriquettes increased with the increase in briquetting pressure.

However, none of the briquettes met with the requirements of TS 12055 in terms of water resistance, since their onset time of dispersion were below 1 hour. Moreover, water resistances of the biobriquettes excluding the biobriquettes prepared from mulberry TSR waste were shorter than that of the lignite briquettes. On the other hand, the mulberry TSR waste containing briquettes showed better water resistance characteristics compared to that of the lignite briquettes. Hence, addition of mulberry TSR waste into the lignite briquettes may increase water resistance of the formed briquettes.

6.2 Effect of Briquetting Pressure on Quality of the Biocoalbriquettes

The effect of briquetting pressure on the quality of the binderless biocoalbriquettes manufactured from the lignite–hazelnut refuse blends was determined in terms of compressive strength, impact strength, and water resistance.

6.2.1 Effect of briquetting pressure on compressive strength of the biocoalbriquettes

In order to determine the effect of briquetting pressure on compressive strength of the binderless biocoalbriquettes, three different mixtures of the lignite and the hazelnut refuse samples were briquetted with no additives by applying three different briquetting pressures. Compressive strength values of these briquettes are shown in **Figure 6.1**.

In the light of these experimental findings, it can be calculated that increasing briquetting pressure from 350 MPa to 700 MPa improved compressive strength of the biocoalbriquettes containing 10, 15, and 20 wt% biomass 13, 46, and 46%, respectively, whilst increasing briquetting pressure from 700 MPa to 1000 MPa raised compressive strength of these biocoalbriquettes 13, 34, and 38%, respectively.

Therefore, it can be reported that compressive strength of the binderless biocoal briquettes increased with the increase in briquetting pressure. Withal, an increase in briquetting pressure of the biocoal briquettes from 700 MPa to 1000 MPa was found to be more effective than that of the briquettes produced from coal or biomass samples with no additives. Kaliyan and Morey [8] reported that under high pressure, natural binding components such as starch, protein, lignin, and pectin in the biomass materials are squeezed out of the particles, which contribute to interparticle bonding.

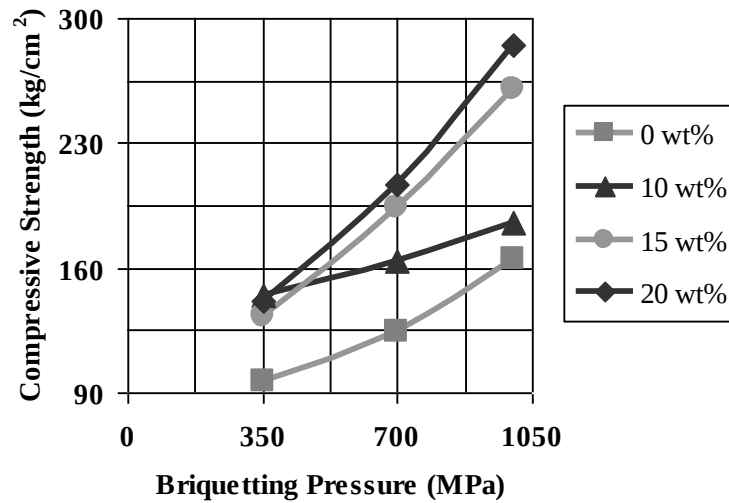


Figure 6.1 : Effect of briquetting pressure on compressive strength of the binderless biocoal briquettes produced from the mixtures of the coal and the hazelnut refuse.

Moreover, all of the briquettes manufactured from lignite–hazelnut refuse blends were met with the requirements of class I briquettes in terms of compressive strength, since minimum acceptable value is 130 kg/cm² according to TS 12055. Therefore, any of the three briquetting pressures can be selected to produce briquettes with proper compressive strength characteristics.

6.2.2 Effect of briquetting pressure on impact strength of the biocoal briquettes

In order to determine the effect of briquetting pressure on impact strength of the binderless biocoal briquettes, three different mixtures of the lignite and the hazelnut refuse samples were briquetted without using binder material under three different briquetting pressures. Impact strength values of these briquettes are shown in **Figure 6.2**.

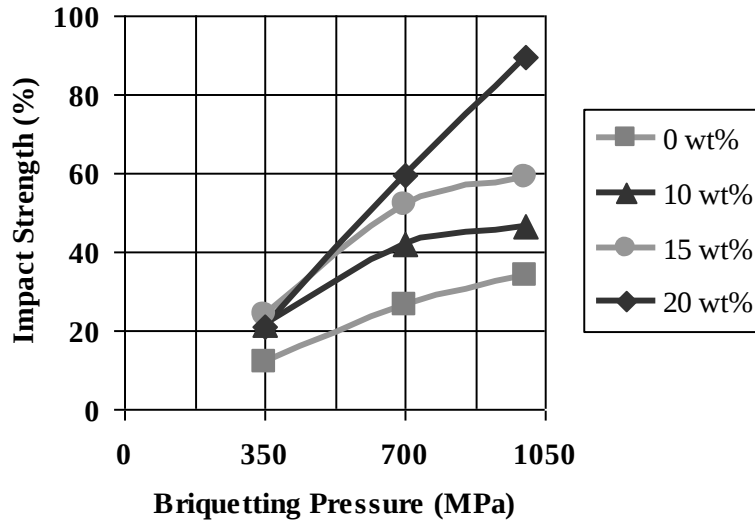


Figure 6.2 : Effect of briquetting pressure on impact strength of the binderless biocoal briquettes produced from the mixtures of the coal and the hazelnut refuse.

According to these experimental findings, it can be reported that increasing briquetting pressure from 350 MPa to 700 MPa enhanced impact strength of the biocoal briquettes containing 10, 15, and 20 wt% biomass 96, 116, and 184%, respectively, whilst increasing briquetting pressure from 700 MPa to 1000 MPa raised impact strength of these biocoal briquettes 10, 14, and 51%, respectively. Therefore, it can be indicated that impact strength of the binderless biocoal briquettes increased with the increase in briquetting pressure. However, none of the briquettes excluding the 20 wt% biomass containing biocoal briquettes prepared under a briquetting pressure of 1000 MPa met with the requirements of TS 12055 in terms of impact strength.

6.2.3 Effect of briquetting pressure on water resistance of the biocoal briquettes

In order to determine the effect of briquetting pressure on water resistance of the binderless biocoal briquettes, three different mixtures of the lignite and the hazelnut refuse samples were briquetted without any binder material by applying three different briquetting pressures. Water resistance values of these briquettes are given in **Figure 6.3**. Water resistance of the formed biocoal briquettes was poor and none of the biocoal briquettes met with the requirements of TS 12055 in terms of water resistance, since their onset time of dispersion were below 1 hour. Adding hazelnut

refuse into the lignite briquettes affected water resistance of the produced biocoal briquettes negatively.

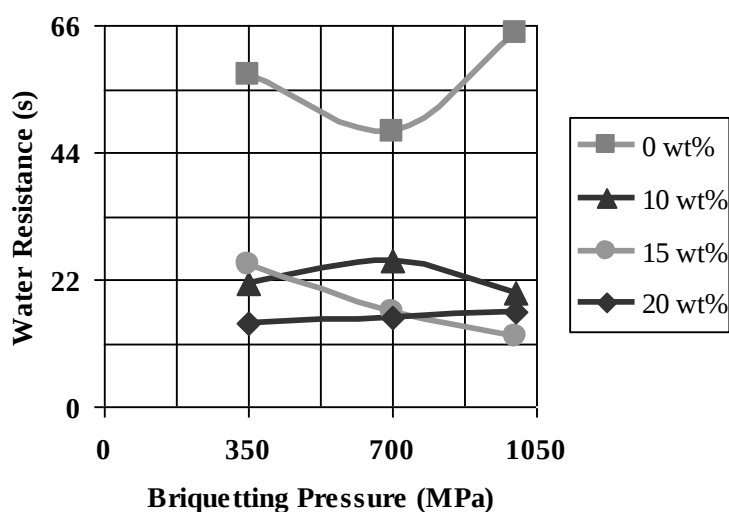


Figure 6.3 : Effect of briquetting pressure on water resistance of the binderless biocoal briquettes produced from the mixtures of the coal and the hazelnut refuse.

6.3 Effects of Biomass Type and Content on Quality of the Biocoal briquettes

The effects of biomass type and content on the quality of the binderless biocoal briquettes manufactured by mixing the lignite sample with various biomass samples in different amounts were determined in terms of compressive strength, impact strength, and water resistance.

6.3.1 Effects of biomass type and content on compressive strength of the biocoal briquettes

In order to determine the effects of biomass type and content on compressive strength of the formed binderless biocoal briquettes, the mixtures of the coal and the four different biomass samples with different biomass contents were briquetted by applying a briquetting pressure of 700 MPa. Compressive strength values of these briquettes are shown in **Table 6.4**.

In the light of these experimental findings, it can be calculated that increasing biomass content from 0 wt% to 10 wt% increased compressive strength of the hazelnut refuse, the grape TSR waste, and the locust TSR waste containing biocoal briquettes 59, 22, and 32%, respectively, whilst increasing biomass content

from 0 wt% to 10 wt% decreased compressive strength of the mulberry TSR waste containing biocoal briquettes 36%. Moreover, an increase in hazelnut refuse content from 0 wt% to 15 wt% raised compressive strength of the formed biocoal briquettes 56%, whereas an increase in hazelnut refuse content from 0 wt% to 20 wt% improved compressive strength of the produced biocoal briquettes 67%.

Table 6.4 : Effects of biomass type and content on compressive strength of the binderless biocoal briquettes.

Biomass Content (wt%)	Compressive Strength (kg/cm ²)			
	TSR Waste			Hazelnut Refuse
	Grape	Locust	Mulberry	
0	124.00	124.00	124.00	124.00
5	162.06	136.59	135.25	–
10	197.28	151.73	79.37	163.68
15	–	–	–	193.89
20	–	–	–	206.48

On the other hand, compressive strength of the binderless biocoal briquettes varied with biomass type. Grape TSR waste, which was followed, respectively, by hazelnut refuse and locust TSR waste, enhanced compressive strength of the biocoal briquettes the most, when added into the lignite briquettes in same amounts, whilst mulberry TSR waste reduced impact strength of the formed biocoal briquettes under same conditions. Ma et al. [121] conducted briquetting experiments using three different coal samples and rice straw at different conditions. Results showed that mechanical performance of the produced briquettes improved with rice straw addition and the reasonable lower limit of biomass content was about 15 wt%.

Furthermore, all of the binderless biocoal briquettes excluding the biocoal briquettes prepared from mulberry TSR waste with a biomass content of 10 wt% were met with the requirements of class I briquettes in terms of compressive strength, since minimum acceptable value is 130 kg/cm² according to TS 12055. Therefore, any of the biomass type and content can be selected to produce briquettes with proper compressive strength characteristics.

6.3.2 Effects of biomass type and content on impact strength of the biocoal briquettes

In order to determine the effects of biomass type and content on impact strength of the binderless biocoal briquettes, the mixtures of the coal and the four different

biomass samples with different biomass contents were briquetted under a briquetting pressure of 700 MPa. Impact strength values of these briquettes are given in **Table 6.5**.

Table 6.5 : Effects of biomass type and content on impact strength of the binderless biocoal briquettes.

Biomass Content (wt%)	Impact Strength (%)			
	TSR Waste			Hazelnut Refuse
	Grape	Locust	Mulberry	
0	26.65	26.65	26.65	26.65
5	24.30	28.92	16.10	–
10	34.93	33.73	16.77	42.40
15	–	–	–	51.87
20	–	–	–	59.32

According to these experimental findings, it can be reported that increasing biomass content from 0 wt% to 10 wt% increased impact strength of the hazelnut refuse, the grape TSR waste, and the locust TSR waste containing biocoal briquettes 58, 31, and 27%, respectively, whilst increasing biomass content from 0 wt% to 10 wt% decreased impact strength of the mulberry TSR waste containing biocoal briquettes 37%. Moreover, an increase in hazelnut refuse content from 0 wt% to 15 wt% raised impact strength of the formed biocoal briquettes 95%, whereas an increase in hazelnut refuse content from 0 wt% to 20 wt% improved impact strength of the produced biocoal briquettes 123%.

On the other hand, impact of the binderless biocoal briquettes varied with biomass type. Hazelnut refuse, which was followed, respectively, by grape TSR waste and locust TSR waste, enhanced impact strength of the biocoal briquettes the most, when added into the lignite briquettes in same amounts, whilst mulberry TSR waste reduced impact strength of the formed biocoal briquettes under same conditions. However, none of the binderless biocoal briquettes were met with the requirements of TS 12055 in terms of impact strength. Kaliyan and Morey [8] reported that biomass constituents such as starch, protein, fiber, and fat are affecting the strength and the durability of the produced briquettes. The commonly observed binding characteristics of these constituents are gelatinization of starch, denaturation of protein, and solubilization and subsequent recrystallization of sugars and salts [148]. Some researchers found that increasing the protein content of biomass increased the hardness and the durability of the briquettes [149–151].

6.3.3 Effects of biomass type and content on water resistance of the biocoal briquettes

In order to determine the effects of biomass type and content on water resistance of the biocoal briquettes, the mixtures of the coal sample and the four different biomass samples with different biomass contents were briquetted by applying a briquetting pressure of 700 MPa. Water resistance values of these briquettes are shown in **Table 6.6**.

Table 6.6 : Effects of biomass type and content on water resistance of the binderless biocoal briquettes.

Biomass Content (wt%)	Water Resistance (s)			
	TSR Waste			Hazelnut Refuse
	Grape	Locust	Mulberry	
0	47.67	47.67	47.67	47.67
5	33.36	33.20	167.07	–
10	27.05	22.80	348.37	25.38
15	–	–	–	16.37
20	–	–	–	15.40

Experimental findings showed that increasing biomass content from 0 wt% to 10 wt% decreased water resistance of the hazelnut refuse, the grape TSR waste, and the locust TSR waste containing biocoal briquettes 47, 43, and 52%, respectively, whilst increasing biomass content from 0 wt% to 10 wt% increased water resistance of the mulberry TSR waste containing biocoal briquettes 631%. Also, an increase in hazelnut refuse content from 0 wt% to 15 wt% reduced water resistance of the formed biocoal briquettes 66%, whereas an increase in hazelnut refuse content from 0 wt% to 20 wt% reduced water resistance of the produced biocoal briquettes 68%. Hence, adding mulberry TSR waste into the lignite briquettes improved water resistance of the formed briquettes, whilst opposite effects were seen in the case of addition of other biomass materials. However, none of the binderless biocoal briquettes were met with the requirements of TS 12055 in terms of water resistance.

6.4 Effect of Briquetting Time on Impact Strength of the Biocoal Briquettes

The effect of briquetting time on impact strength of the binderless biocoal briquettes was studied for the purpose of investigating the possibility of enhancing impact strength of the briquettes by changing the briquetting time. In order to determine the

effect of briquetting time, 20 wt% hazelnut refuse or 10 wt% TSR waste containing lignite–biomass blends were briquetted under a briquetting pressure of 700 MPa by changing the briquetting time in the range of 0–60 s. Impact strength values of these briquettes are given in **Figure 6.4**.

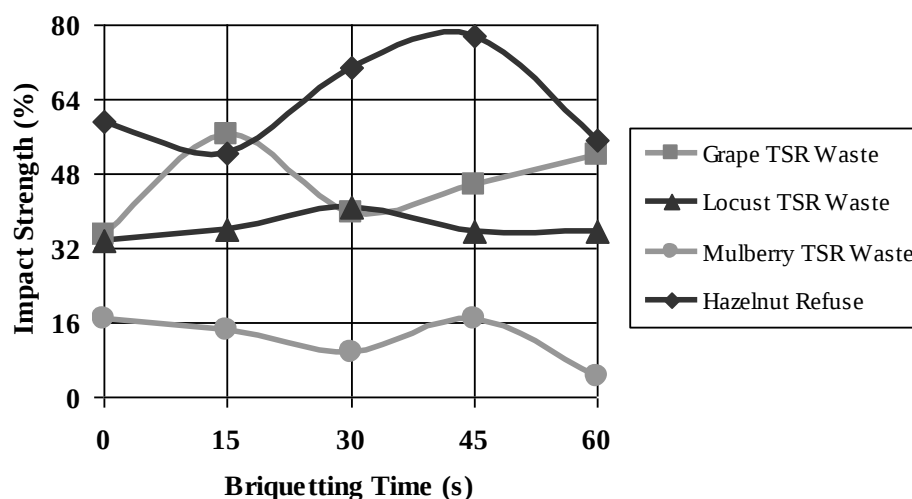


Figure 6.4 : Effect of briquetting time on impact strength of the binderless biocoal briquettes.

According to these experimental findings, it can be reported that increasing briquetting time from 0 s to 15 s increased impact strength of the grape TSR waste containing biocoal briquettes the most (61%), whilst increasing briquetting time from 0 s to 30 s raised impact strength of the locust TSR waste containing biocoal briquettes the most (21%). On the other hand, an increase in briquetting time from 0 s to 45 s increased impact strength of the hazelnut refuse containing biocoal briquettes the most (31%). However, increasing briquetting time negatively affected impact strength of the mulberry TSR waste containing biocoal briquettes. Besides, none of these biocoal briquettes were met with the requirements of TS 12055 in terms of impact strength.

6.5 Effect of Binder Type on Quality of the Biocoal Briquettes

The effect of binder type on the quality of the produced biocoal briquettes was determined in terms of compressive strength, impact strength, and water resistance.

6.5.1 Effect of binder type on compressive strength of the biocoal briquettes

In order to determine the effect of binder type on compressive strength of the biocoal briquettes, lignite–biomass blends with fixed coal:biomass ratios were briquetted under a briquetting pressure of 700 MPa by using three different binder materials. Compressive strength values of these briquettes are shown in **Table 6.7**.

Table 6.7 : Effect of binder type on compressive strength of the biocoal briquettes.

Biomass Type	Coal:Biomass Ratio (w/w)	Compressive Strength (kg/cm ²)			
		Binder Type and Content (wt%)			
		Binderless	Molasses (10 wt%)	Linobind (4 wt%)	Plant root solution (10 wt%)
Hazelnut Refuse	80:20	206.48	118.98	307.20	92.59
Grape TSR Waste	90:10	197.28	136.80	213.83	143.38
Locust TSR Waste	90:10	151.73	75.69	117.28	56.59
Mulberry TSR Waste	90:10	79.37	49.02	121.59	96.48

In the light of these experimental findings, it can be reported that adding molasses into the hazelnut refuse, the grape TSR waste, the locust TSR waste, and the mulberry TSR waste containing biocoal briquettes reduced compressive strength of the formed biocoal briquettes 42, 31, 50, and 38%, respectively.

By the same token, compressive strength of the hazelnut refuse, the grape TSR waste, and the mulberry TSR waste containing biocoal briquettes increased 49, 8, and 53%, respectively, with the use of linobind as a binder material, whilst compressive strength of the biocoal briquettes prepared from locust TSR waste decreased 23% under same conditions. Taulbee et al. [22] evaluated over 50 binder reagents to briquette fine bituminous coal–sawdust blends using a hydraulic press, and identified guar gum and wheat starch as the best performing binders.

Withal, compressive strength of the hazelnut refuse, the grape TSR waste, and the locust TSR waste containing biocoal briquettes reduced 55, 27, and 63%, respectively, and compressive strength of the biocoal briquettes manufactured from mulberry TSR waste improved 22% in the case of adding plant root solution as a binder material.

On the other hand, use of linobind as a binder material improved compressive strength of the hazelnut refuse and the grape TSR waste containing biocoal briquettes, whereas addition of molasses and plant root solution reduced compressive strength of

these biocoal briquettes. Moreover, adding linobind and plant root solution increased compressive strength of the mulberry TSR waste containing biocoal briquettes, whereas using molasses as a binder decreased compressive strength of these biocoal briquettes. However, all of these three binder materials negatively affected compressive strength of the locust TSR waste containing biocoal briquettes.

Furthermore, the molasses added biocoal briquettes produced from coal–hazelnut refuse blends and the linobind added biocoal briquettes manufactured from coal–locust TSR waste or coal–mulberry TSR waste blends were found to be class II briquettes with respect to TS 12055 in terms of compressive strength, whereas the linobind added biocoal briquettes prepared from coal–hazelnut refuse blends met with the requirements of class I briquettes. Additionally, the compressive strength of the grape TSR waste containing biocoal briquettes produced with the use of any of the three binder materials were accordance with the class I briquettes according to TS 12055 in terms of compressive strength.

With respect to the experimental facts, linobind can be concluded to be the best binder in terms of compressive strength for the hazelnut refuse, the grape TSR waste and the mulberry TSR waste containing biocoal briquettes.

6.5.2 Effect of binder type on impact strength of the biocoal briquettes

In order to determine the effect of binder type on impact strength of the biocoal briquettes, lignite–biomass blends with fixed coal:biomass ratios were briquetted under a briquetting pressure of 700 MPa by using three different binder materials. Impact strength values of these briquettes are given in **Table 6.8**.

Table 6.8 : Effect of binder type on impact strength of the biocoal briquettes.

Biomass Type	Coal: Biomass Ratio (w/w)	Impact Strength (%)			
		Binder Type and Content (wt%)			
		Binderless	Molasses (10 wt%)	Linobind (4 wt%)	Plant root solution (10 wt%)
Hazelnut Refuse	80:20	59.32	73.29	83.14	92.48
Grape TSR Waste	90:10	34.93	17.92	39.99	58.13
Locust TSR Waste	90:10	33.73	7.26	31.52	13.79
Mulberry TSR Waste	90:10	16.77	3.96	15.85	49.08

According to these experimental findings, it can be reported that adding molasses into the hazelnut refuse containing biocoal briquettes raised impact strength of the

formed biocoal briquettes 24%, whereas addition of molasses into the grape TSR waste, the locust TSR waste, and the mulberry TSR waste containing biocoal briquettes reduced impact strength of these biocoal briquettes 49, 78, and 76%, respectively.

In the literature there are some contradictory results about the binder effects of molasses. Yaman et al. [4] briquetted a lignite sample containing 15 wt% moisture under 250 MPa pressure without using binder. The shatter index, compressive strength and water resistance of the produced briquettes were determined as 5026, 17.6 MPa, and 4 min, respectively. The addition of molasses (15 wt%) to this lignite sample effected the mechanical strength of the briquettes negatively. Gürbüz–Beker and Küçükbayrak [87] briquetted a lignite sample with and without binder material. Without binder material, the production of the briquettes with acceptable strength and water resistance was not possible. Using molasses as binder material (12 wt%) at a briquetting pressure of 200 MPa gave stronger briquettes with a shatter index of 2572, and a compressive strength of 12.2 MPa.

By the same token, impact strength of the hazelnut refuse and the grape TSR waste containing biocoal briquettes increased 40 and 15%, respectively, with the use of linobind as a binder material, whilst impact strength of the locust TSR waste and the mulberry TSR waste containing biocoal briquettes decreased 7 and 5%, respectively, under same conditions.

Withal, impact strength of the hazelnut refuse, the grape TSR waste, and the mulberry TSR waste containing biocoal briquettes improved 56, 66, and 193%, respectively, and impact strength of the biocoal briquettes manufactured from coal–locust TSR waste blend reduced 59% in the case of adding plant root solution as a binder material.

On the other hand, addition of these three binders enhanced impact strength of the hazelnut refuse containing biocoal briquettes. However, biocoal briquettes produced with the use of molasses did not meet with the requirements of TS 12055 in respect of impact strength. Nevertheless, biocoal briquettes manufactured by adding linobind and plant root solution were found to be class II and class I briquettes, respectively, according to the impact strength limitations of TS 12055.

Moreover, addition of linobind and plant root solution improved impact strength of the grape TSR waste containing biocoal briquettes, whereas use of molasses as a binder material reduced impact strength of these biocoal briquettes. Furthermore, adding plant root solution increased impact strength of the mulberry TSR waste containing biocoal briquettes, whereas using molasses and linobind as binders decreased impact strength of these biocoal briquettes. With respect to the experimental facts, plant root solution can be concluded to be the best binder in terms of impact strength for the grape TSR waste and the mulberry TSR waste containing biocoal briquettes. However, all of these three binder materials negatively affected impact strength of the locust TSR waste containing biocoal briquettes. Besides, none of the biocoal briquettes prepared from coal–TSR waste blends met with the requirements of TS 12055 in terms of impact strength.

6.5.3 Effect of binder type on water resistance of the biocoal briquettes

In order to determine the effect of binder type on water resistance of the biocoal briquettes, lignite–biomass blends with fixed coal:biomass ratios were briquetted under a briquetting pressure of 700 MPa by using three different binder materials. Water resistance values of these briquettes are shown in **Table 6.9**.

Table 6.9 : Effect of binder type on water resistance of the biocoal briquettes.

Biomass Type	Coal:Biomass Ratio (w/w)	Water Resistance (s)			
		Binder Type and Content (wt%)			
		Binderless	Molasses (10 wt%)	Linobind (4 wt%)	Plant root solution (10 wt%)
Hazelnut Refuse	80:20	15.40	12.96	16.47	2470.44
Grape TSR Waste	90:10	27.05	10.66	85.37	5950.28
Locust TSR Waste	90:10	22.80	18.01	44.16	43.39
Mulberry TSR Waste	90:10	348.37	48.08	4598.19	22350.75

Experimental findings showed that adding molasses into the hazelnut refuse, the grape TSR waste, the locust TSR waste, and the mulberry TSR waste containing biocoal briquettes reduced water resistance of the formed biocoal briquettes 16, 61, 21, and 95%, respectively, whereas addition of linobind into these biocoal briquettes raised water resistance of the produced biocoal briquettes 7, 216, 94, and 1220%, respectively. By the same token, water resistance of these biocoal briquettes increased 15942, 21897, 90, and 6316%, respectively, with the use of plant root solution as a binder material. Therefore, it can be indicated that water resistance of the formed

biocoal briquettes enhanced when linobind or plant root solution were added into these briquettes as binding agents, whilst opposite effects were seen in the case of using molasses. Withal, addition of plant root solution was more effective compared to adding linobind.

7. CONCLUSION AND RECOMMENDATIONS

Firstly, the effect of briquetting pressure on quality of the briquettes manufactured from lignite or biomass samples was studied, and obtained results are listed below:

- None of the lignite briquettes produced under briquetting pressures of 350, 700, and 1000 MPa had sufficient impact strength and water resistance according to TS 12055, although compressive strength of the lignite briquettes prepared by applying briquetting pressures of 700 and 1000 MPa met with the requirements of class II and class I briquettes, respectively.
- The hazelnut refuse biobriquettes manufactured under a briquetting pressure of 350 MPa were not acceptable with respect to TS 12055 in terms of compressive strength, impact strength, and water resistance. However, compressive strength and impact strength of the biobriquettes produced from hazelnut refuse by applying briquetting pressures of 700 and 1000 MPa matched with the requirements of class I briquettes.
- The grape TSR waste biobriquettes prepared under a briquetting pressure of 350 MPa had insufficient impact strength and water resistance according to TS 12055. However, compressive strength and impact strength of the biobriquettes manufactured from grape TSR waste by applying briquetting pressures of 700 and 1000 MPa met with the requirements of class I briquettes.
- None of the locust TSR waste biobriquettes produced under briquetting pressures of 350, 700, and 1000 MPa was acceptable with respect to TS 12055 in terms of compressive strength, impact strength, and water resistance.
- All of the mulberry TSR waste biobriquettes prepared by applying briquetting pressures of 350, 700, and 1000 MPa were unacceptable with respect to TS 12055 in terms of compressive strength and water

resistance, although impact strength of these biobriquettes were well matched with the requirements of class I briquettes.

- An increase in briquetting pressure from 350 MPa to 700 MPa was more effective than increasing it from 700 MPa to 1000 MPa with respect to three quality parameters of the briquettes manufactured from lignite or biomass samples.

Secondly, the effects of biomass type and content on the quality of the binderless biocoalbriquettes are investigated, and obtained results are summarized below:

- None of the 10, 15, and 20 wt% hazelnut refuse containing biocoalbriquettes produced under briquetting pressures of 350 and 700 MPa had sufficient impact strength and water resistance according to TS 12055, although compressive strength of these biocoalbriquettes met with the requirements of class I briquettes.
- None of the 10 and 15 wt% hazelnut refuse containing biocoalbriquettes prepared under a briquetting pressure of 1000 MPa was acceptable with respect to TS 12055 in terms of impact strength and water resistance, although compressive strength of these biocoalbriquettes matched with the requirements of class I briquettes.
- Compressive strength and impact strength of the 20 wt% hazelnut refuse containing biocoalbriquettes manufactured under a briquetting pressure of 1000 MPa was accordance with the requirements for class I briquettes according to TS 12055. However, water resistance of the formed biocoalbriquettes did not met with the requirements of TS 12055.
- None of the 5 and 10 wt% TSR waste containing biocoalbriquettes prepared under a briquetting pressure of 700 MPa had sufficient impact strength and water resistance according to TS 12055, although compressive strength of these biocoalbriquettes matched with the requirements of class I briquettes.
- Addition of hazelnut refuse, grape TSR waste, or locust TSR waste into the lignite briquettes improved compressive strength and impact strength of the formed biocoalbriquettes, and reduced water resistance of the

produced biocoal briquettes. However, opposite effects were seen in the case of adding mulberry TSR waste into the lignite briquettes.

Thirdly, the effect of briquetting time on the impact strength of the binderless biocoal briquettes was studied, and obtained results are shown below:

- None of the biocoal briquettes manufactured by applying a briquetting pressure of 700 MPa for 0–60 s from the lignite–biomass blends containing 10 wt% TSR waste or 20 wt% hazelnut refuse was acceptable with respect to TS 12055 in terms of impact strength.

Lastly, the effect of binder type on the quality of the biocoal briquettes was examined, and obtained results are given below:

- The 10 wt% molasses added biocoal briquettes prepared with a lignite:hazelnut refuse ratio of 80:20 (wt%) under a briquetting pressure of 700 MPa was unacceptable with respect to TS 12055 in terms of impact strength and water resistance, although compressive strength of the formed briquettes were well matched with the requirements of class II briquettes.
- The 4 wt% linobind added biocoal briquettes produced with a lignite:hazelnut refuse ratio of 80:20 (wt%) by applying a briquetting pressure of 700 MPa had insufficient water resistance according to TS 12055, although compressive strength and impact strength of the formed briquettes met with the requirements of class I and class II briquettes, respectively.
- The 10 wt% plant root solution added biocoal briquettes manufactured with a lignite:hazelnut refuse ratio of 80:20 (wt%) under a briquetting pressure of 700 MPa were unacceptable with respect to TS 12055 in terms of compressive strength and water resistance, although impact strength of the formed briquettes were well matched with the requirements of class I briquettes.
- None of the binder material added biocoal briquettes prepared with a lignite:grape TSR waste ratio of 90:10 (wt%) under a briquetting pressure of 700 MPa was acceptable with respect to TS 12055 in terms of impact

strength, although compressive strength of the formed briquettes were well matched with the requirements of class I briquettes. Also, only the grape TSR waste containing biocoal briquettes produced with the use of plant root solution had a water resistance longer than 1 hour.

- None of the 10 wt% molasses added biocoal briquettes manufactured from locust or mulberry TSR waste with a lignite:TSR waste ratio of 90:10 (wt%) under a briquetting pressure of 700 MPa had sufficient compressive strength, impact strength, and water resistance according to TS 12055.
- The 4 wt% linobind added biocoal briquettes prepared from locust or mulberry TSR waste with a lignite:TSR waste ratio of 90:10 (wt%) under a briquetting pressure of 700 MPa were unacceptable with respect to TS 12055 in terms of impact strength, although compressive strength of the formed briquettes were well matched with the requirements of class I briquettes. Also, only water resistance of the mulberry TSR waste containing biocoal briquette was longer than 1 hour.
- None of the 10 wt% plant root solution added biocoal briquettes prepared from locust or mulberry TSR waste with a lignite:TSR waste ratio of 90:10 (wt%) under a briquetting pressure of 700 MPa met with the requirements of TS 12055 in terms of compressive strength and impact strength. Also, only the mulberry TSR waste containing biocoal briquette had a water resistance longer than 1 hour.
- Addition of molasses reduced compressive strength, impact strength (excluding the hazelnut refuse containing biocoal briquettes), and water resistance of the formed biocoal briquettes.
- Using linobind as a binder material improved compressive strength (except for the locust TSR waste containing biocoal briquettes) and water resistance of the produced biocoal briquettes. However, its effect on impact strength varied due to the type of biomass.
- Adding plant root solution enhanced impact strength (excluding the locust TSR waste containing biocoal briquettes) and water resistance of the formed biocoal briquettes, and decreased compressive strength of the

produced biocoal briquettes (except for the mulberry TSR waste containing biocoal briquettes).

Moreover, the hazelnut refuse briquettes and the grape TSR waste briquettes prepared under briquetting pressures of 700 and 1000 MPa, and the 20 wt% hazelnut refuse containing biocoal briquettes manufactured under a briquetting pressure of 700 MPa met with the requirements of TS 12055 for class I briquettes in terms of compressive strength and impact strength, whilst compressive strength and impact strength of the 4 wt% linobind added biocoal briquettes produced with a lignite:hazelnut refuse ratio of 80:20 (wt%) under a briquetting pressure of 700 MPa were accordance with the limitations of TS 12055 for class II briquettes. Since these briquettes were lack of resistance to water, some further researches can be carried out to fulfill the requirements of the standards. Combustion characteristics (i.e. ignition temperature, burnout time, emissions etc.), fuel efficiency, and process feasibility can also be investigated.

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