Biomass briquetting technology is one of the effective utilization technologies of biomass energy. It refers to the processing of various agricultural and forestry wastes into various fuel products with certain shape and density under certain temperature and pressure.

During the briquetting process, the particles undergo a stage of rearrangement, mechanical deformation, plastic rheology and density increase. The briquette quality is affected by the chemical composition of the internal raw materials and the external briquetting parameters, and the force and particle binding mechanism.

Briquetting process

In the briquetting process, it can be divided into four stages according to the deformation of the raw materials.

1. Loose phase (a)

In order to overcome the gap between the raw materials, a certain extent of the air in the raw material is excluded, and the pressure and deformation are linear, and a small pressure increase can obtain a large deformation increment.

2. Transition phase (b)

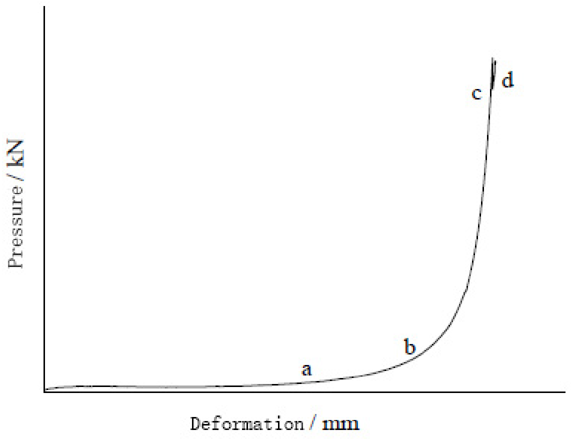
When the pressure increases, the large particles break into small particles, which are elastically deformed and dominate. The internal voids of the particles are filled, and the pressure and deformation are exponential.

3. Compaction phase (c)

The raw material mainly undergoes plastic deformation, and the particles break or deform in the deformation: the direction of the principal principal stress, the particles are fully extended, and the particles are closely combined by the meshing method; the direction of the parallel principal stress is thinned, and the particles are tightly bonded by the fitting method. The briquette is basically formed, and the pressure is related to the plastic deformation of the raw material.

4. Shift stage (d)

The raw material undergoes plasticity and elastic (viscous) deformation, and is mainly composed of elastic (viscous) deformation. Stress relaxation and creep occur in the raw materials, and the pressure drops significantly.



Particle combining way

There are two theories about the way in which the shaped briquette particles are combined:

1. The distance between the particles is close enough to be combined by attraction. During the briquetting process, the electrostatic attraction force generated by the interparticle or internal friction enables the particles to be bonded to each other. When the distance between particles is less than 0.1 μm, van der Waals force becomes the main attraction of interparticle bonding.

2. The particles are combined by a "solid bridge" structure. Some substances or additives in the raw materials, due to chemical reaction, crystallization or solidification, cross-link together when the particles are in contact with each other to form a "solid bridge" structure, which becomes the main way of bonding between particles.

Studies have confirmed that lignin, carbohydrates, starch, protein and fat in corn stalks and switchgrass itself soften or deform, forming a "solid bridge" structure. In addition, the addition of discarded wrap fibers to the saw dust can form a "solid bridge" structure with better mechanical durability.

Further study on the effects of adding rice straw, wheat straw, rubber leaves and nylon on the saw dust briquetting, it was found that rice straw and rubber leaves promoted the physical properties of the pellets, because rice straw, rubber leaves and saw dust belonged to the hydrophilic raw materials, which can effectively entangle each other to form a "solid bridge" structure. Wheat straw and nylon are hydrophobic raw materials, which have a negative effect on improving the quality of the briquettes.

Lignin

Thermal transition characteristics

Biomass is a natural high molecular polymer whose thermal transition properties refer to the glass transition temperature (Tg) and melting temperature. The glass transition temperature refers to the temperature at which the polymer softens and changes from a glassy state to a plastic state. The polymer consists of structural monomers with different molecular weights and chain lengths. The glass transition occurs in a temperature range and is an important property of the polymer. The melting temperature refers to the temperature at which the polymer transitions from a solid to a liquid.

The thermal transition properties of lignin play a key role in the briquetting process.

Below the glass transition temperature, due to the cohesive force formed by the valence bond and the secondary bond, it exhibits higher mechanical strength and a larger elastic modulus; above the glass transition temperature, the lignin molecule partially rotates or shifts gradually. It becomes a thermal expansion movement of molecules, which has enhanced fluidity and a large viscosity.

The glass transition temperature of lignin depends on its source and is related to the type, moisture content, and extraction process.

Studies have shown that hardwood lignin has more acetyl, methoxy structure and a small amount of phenolic hydroxyl structure, and its glass transition temperature is lower than that of softwood. The glass transition temperature of wheat straw also has an effect on the formed particles. When the moisture content is 8%, the glass transition temperatures of wheat straw and wheat straw (extracted by n-hexane) are 53 ° C and 63 ° C. The increase of water will lower the glass transition temperature, because water can act as a plasticizer, lignin – The hydrogen bond junction between the lignin molecules is replaced by a lignin-water linkage.

Lignin bonding

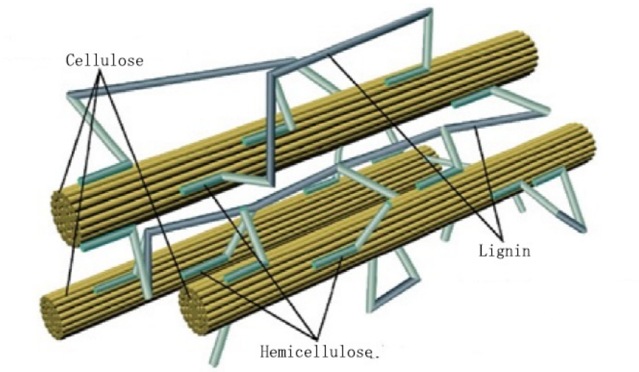
During the briquetting process, the lignin undergoes thermal transformation and then bonds and solidifies and fills, which is the main component of the biomass itself. At 70 ~ 110 °C, the lignin begins to soften and has a certain viscosity. At 200 ~ 300 °C, it will melt and the viscosity will increase. At this time, under a certain pressure, cellulose, hemicellulose, and the like in the raw material are mutually attracted and entangled and bonded by molecules.

Lignin structure

The hydroxyl group, especially the phenolic hydroxyl group, easily forms a rich hydrogen bond structure, which is favorable for promoting the bonding formation and increasing the mechanical strength of the particles. The lignin content of saw dust and hardwood sawdust is similar (according to the US Renewable Energy Laboratory database, eucalyptus sawdust contain lignin 26.91% ~ 28.16%, hardwood sawdust contain lignin 23.87% ~ 28.55%), but the fact is eucalyptus sawdust has high energy consumption and low density and strength after briquetting. This may be because lignin is dominated by syringyl-based structural units in eucalyptus, while lignin is dominated by guaiac wood-based structural units in hardwood. The lignin bonding index of the syringyl structural unit is lower than that of the guaiac w ood-based structural unit makes the briquetting effect quite different.

Chemical composition of raw materials

The biomass is complex in structure, including cellulose, hemicellulose, and lignin, as w ell as extracts and ash. Different components have different roles in the briquetting process. Different types of biomass components and structures are different, and the briquetting difficulty and effect is also quite different.



CELLULOSE

Cellulose is a highly ordered linear polymer formed by the coupling of hundreds to thousands of D-glucose by β-1,4 glycosidic linkages. The smallest repeating unit is cellobiose ($C6H10O5$)n. In plant cells, cellulose forms crystalline microfibers, microfibers are surrounded by amorphous fibers, and cellulose molecules have crystalline and amorphous regions. It can not be used as a binder due to the cellulose crystal structure and abundant hydrogen bonds, but it becomes softer after heating. The filaments joined by hydrogen bonds act like a "rebar" in the briquette and become the "skeleton" of the briquette. Increase the moisture content, pressure and temperature w ithin a certain range to improve the quality of biomass briquettes.

HEMICELLULOSE

Hemicellulose is a polysaccharide obtained by polymerizing different kinds of monosaccharides, and its polymer chain is amorphous and has a short chain. In hardw ood, the hemicellulose backbone is formed by xylose units linked by β-1,4 glycosidic bonds, and the branches are composed of β-1,2 glycosidic linkages and 4-O-methylglucuronic acid linkages. The hemicellulose backbone of cork contains less acetyl groups but has arabinofuranose side chains attached to the backbone. In the briquetting process, hemicellulose can be degraded into lignin under the action of pressure and hydrolysis, and acts as a binder.

LIGNIN

Lignin is an aromatic compound having a three-dimensional polyphenol netw ork structure obtained by polymerizing guaiacol-based, syringyl-based, p-hydroxybenzene-like phenylpropane monomers. The content of the three monomers is different depending on the raw materials. In the softwood, the guaiac wood-based structural unit is the main component, and the hardw ood is dominated by the syringyl-based structural unit.

Some studies on the effects of lignin content on briquetting:

- Temperature above 140 °C can increase the bonding strength of lignin;
- The raw material component is the key factor affecting the quality of the granule. The granules w ith high lignin content and low extraction content have better physical quality.
- For fresh and stored bark, saw dust, and harvesting residue materials, particles with high lignin content have good durability;
- The higher the lignin content, the better the internal bonding of the particles, the higher the temperature than the glass transition temperature, and the mechanical strength of the particles increases;
- Lignin is a viscose substance with poor internal strength. It can bond in the crystal structure of the wood polymer w ithin a certain range, but its content exceeds the critical value. Excessive gelatinous substances accumulate betw een the crystals, will reduce the particles strength and durability;
- For hardw ood and softwood, the relationship betw een lignin content and particle durability is not significant.

Starch

Starch is a D-glucose polymer, w hich is divided into branched amylopectin and unbranched amylose, and is insoluble in w ater at normal temperature. During the briquetting process, under the action of certain temperature, moisture, pressure and compression time, starch gelatinization phenomenon (irreversible) occurs, which acts as a binder and a lubricant to facilitate the discharge of briquette from the mold.
There are tw o mechanisms for starch gelatinization:
1 Under the action of moisture and temperature, the crystal structure is damaged;
2 During the compression process, shearing and squeezing cause the starch granules to break. The higher the degree of starch gelatinization, the more obvious the bonding effect and the greater the mechanical strength of the briquette.

Protein

Under certain temperature and moisture conditions, the protein in the raw material w ill undergo a denaturation process, and proteins, fats and starches will be converted into new substances, which will help to improve the adhesion of the protein. Studies have show n that increasing the protein content of the raw material can improve the mechanical durability of the product, and the undenatured protein can improve the physical quality of the product more than the denatured protein. When the raw material contains enough natural protein, it can enhance its function as a binder. Raw materials w ith higher starch and protein content have better mechanical durability than products made from raw materials containing only cellulose. For raw materials containing only cellulose, the optimum moisture content is 8% to 12%, w hile raw materials w ith higher starch and protein content. The optimal moisture content can reach 20%. Proteins extracted from soybean, wheat, rye and barley can promote the formation of the protein. The protein extracted from corn is the opposite. Crude protein is more favorable for promoting briquetting than denatured protein. Compared w ith starch, whether it is raw starch or gelatinized starch, the promotion of crude protein is better.

FAT

The fat in the raw material mainly acts as a lubricant during the briquetting process, and a small amount of fat promotes the briquetting, because the natural fat in the cell w all is extruded during the pressing process, acting as a "solid bridge" to improve durability. How ever, too much fat hinders the bonding betw een particles, because fat is distributed betw een particles, and its hydrophobicity can inhibit the bonding of other w ater-soluble components (such as lignin, starch, protein, etc.) and reduce the bonding strength betw een particles. The fat content of more than 6.5% w ill make the briquette of poor durability, w hich is not conducive to improving the bonding effect of starch and protein.

Briquetting parameters

PRESSURE

Pressure is a necessary condition for briquetting. Within a certain initial pressure range, the pressure and product density are basically linear. Exceeding this pressure range, the pressure and product density are exponential. After the pressure reaches a certain value, the product density does not increase w ith pressure. The pressure is exponentially related to the length of the particles, and an increase in temperature reduces the required pressure.

MOISTURE

Moisture is an important parameter to be controlled during the briquetting process. Moisture can low er the glass transition temperature, promote the formation of "solid bridge" structure, and increase the contact area betw een particles.

Moisture is a natural binder and lubricant. A certain amount of w ater can form a film betw een particles, increasing the contact area and interaction force between particles (Vandelwald force). The film can also reduce the friction betw een the raw material and mold as w ell as the raw material particles, reducing energy consumption.

How ever, too much moisture w ill reduce the quality of the briquette, as too much moisture can not be absorbed by the particles and adhere to the surface, making the particles difficult to briquette. The optimum moisture content required for different raw materials is different. If the moisture is greater or low er than the optimum value, the product quality w ill be reduced. Studies show s, the optimum moisture content of the fiber raw materials is 8% to 12%. The product quality is best w hen the moisture of rice straw is 8% ~ 12% as w ell.

PARTICLE SIZE

Particle size is also one of the factors affecting the formation. The smaller the particle size, the easier it is to be compressed, and the better the product quality. Uneven particle size, large morphological differences, or large particle sizes result in reduced product density and strength, and cracks on the surface and inside. Studies show s that the smaller the particle size, the greater the density of the shaped particles. In fact, if the raw materials w ith different particle sizes are mixed and molded, the quality of the products will be better, because the fibers or tw isted flakes in the particles have bending and winding properties, and they entangle each other when gathered to form a "solid bridge" structure, thereby improving product quality.

TEMPERATURE

During the briquetting process, the temperature is increased to soften the lignin and make it with bonding effect, and the raw material itself can be softened and easily compressed. However, the temperature should not be too high, otherwise the raw material is carbonized seriously and the briquetting fails. The optimum temperature for briquetting different raw materials is generally 80 to 150 °C.

There is also an interaction between moisture and temperature. Take the corn straw as an example, in order to reduce the energy cost on briquetting, certain temperature and moisture should be set, when the temperature is lower than 100 °C, the moisture should be lowered. When the temperature is higher than 100 °C, the moisture should be increased, this will keep the energy consumption on a certain point. The energy consumption has the lowest point at 100 °C.