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A STUDY OF FORMING MECHANISM IN BRIQUETTES MADE FROM CARAGANA KORSHINSKII KOM

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ABSTRACT

Caragana korshinskii Kom is an important feedstock for producing high-quality solid fuel which possess excellent physical characteristic. In this study, the bonding mechanisms and failure mechanisms at microscopic perspective were analyzed combining the physical characteristics of briquettes. The Scanning electron microscope (SEM) images showed that bonding between particles was created through short-range forces and solid bridge. The short-range forces in fine particles could increase the density of briquette but could not resist the disruptive forces. The solid bridges were made mainly by natural binders such as lignin and mechanical interlocking in the fibers, flat shaped particles and bulky particles. The appropriate moisture and temperature in the range of glass transition is essential to produce high quality briquettes. The interface failure of solid bridge caused the destruction of bulky particles; the cohesive failure caused the destruction of the fine particles

Keywords: Caragana korshinskii Kom, briquette, bonding mechanism, failure mechanism, physical characteristic

1. INTRODUCTION

Densification technology of biomass transforms irregular biomass materials of low bulk density into high-density, well-define shaped and sized solid fuel, which reduced greatly the handling, storage and transportation costs of biomass materials. High-quality biomass solid fuel is required to have excellent physical properties which will ensure the integrity of the fuel during storage, handling, transportation and other environments. Only in this way biomass fuels would gain popularity in the civil usejust like fossil fuels (e.g., coal), allowing automatic feeding in a continuous heating system, such as a power plant, improving the economic benefits of the biomass solid fuel industry [1,2].

The physical characteristics of biomass solid fuel depend on the bonding strength among the particles, and the bonding strength is affected by different bonding mechanism. Chung [3] proposed an explanation of particles bonding at a micro level, deducing two standards related to strongly bonding molecules: close molecular contact less than 9 Å (necessary condition); the minimum potential energy to produce the greatest attraction (sufficient conditions). The interaction between molecules is the motive power of bonding. Chemical bonding is established, when the maximum attraction is close to the minimum potential energy. Pressure, heat (above

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the glass transition temperature) and solvents (such as water) are necessary to promote bonding by increasing the contact between molecules.

In the present studies, Rumpf and Pietsch[4, 5]divided the bonding forces between particles into two categories: (1)Bonding without a solid bridge,i.e., attraction forces between particles help bond the particles. If the distance between the molecules is close enough, short-range force such as molecular force (valence force, i.e., chemical bonding, hydrogen bonding, and van der Waals force), electrostatic force and magnetic force can cause the solid particles to adhere to each other. Valence forcesare only effective when the particle distance is approximately 10 Å. Van der Waals forces, which are effective when the distance between particles is less than 0.1 μm, make the greatest contribution to the intermolecular attraction. Electrostatic forces play an important role in forming the bonds when excess charge or electrical double layer is generatedduring grinding or friction between particles. Magnetic forces in the powder promote particle bonding. When the particle size or distance increases, the effectiveness of the short-range force is significantly reduced.(2) Bonding with a solid bridge. Solid bridges may be developed by: (i) diffusion of molecules inter-particles due to the application of high pressure and temperatures, (ii) crystallization of some ingredients, chemical reaction, hardening of binders, and solidification of melted components, (iii) mechanical interlocking bond developed by the interlocked or folded fibers, flat shaped particles, and bulky particles during the compression process, (iv) adhesion forces and cohesion forces generated by highly viscous binders that are very similar to solid bridges, and (v) liquid bridges that hold particles together by capillary and viscous forces caused by spread in the interstices between primary particles of free moisture. Subsequently, the liquid evaporates from the bridges to leave solid bridges.

The natural binders in biomass are hemicellulose, lignin, protein, starch, fat, water-soluble carbohydrate (WSC), etc.; these binders can be activated under conditions of high temperature and suitable humidity to perform the bonding function. These physical and chemical changes will affect the bonding characteristics of biomass particles. The lignin and hemicellulose are essentially thermoplastic polymers and change their state from a hard glassy to a soft rubbery state, plastic deformation can occur easily at low pressure during glass transition [6, 7]. Back[8] found that plasticization of wood polymer with glass transition temperature would result in the formation of adequate bonding area, especially in the region lacking a binder. During the hot extrusion process of wood materials, the hydrogen bonding of lignin and cellulose is the primary bonding mechanism. Bonding between fibers mainly occurs by covalent bonding. Covalent bonding is the strongest, followed by hydrogen bonding and van der Waals interactions in chemical bonding. The composite effect of temperature, moisture and shear will lead to enhance of abrasive resistance resulting from the starch gelatinization and the promotion of bonding by protein denaturation [9-11].The natural fat in the plant cell wall that is extruded from the cells acts as a binder between the particles and forms a solid bridge, which will have a beneficial effect on the durability of the particles[11].

In this study, the bonding mechanism of solid fuel made from Caragana korshinskii Kom was studied at microscope level, analyzed the effect of the natural binder and the bonding mechanism

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of Caragana korshinskii Kom under different conditions on the physical properties of solid fuel. In addition, the failure mechanism of solid fuel in the destruction process by external force was studied to offer an insight into interaction mechanism between particles. This will provide a reference for the selection of the optimum processing conditions for producing strong briquettes and low process energy consumption.

2 MATERIALS AND METHODS

2.1 MATERIALS

In this study, eight-year-old and above C. korshinskii Kom was used as a biomass material. Thematerialwas grown in the Dingxiang, Shanxi,China. After harvesting, the C. korshinskii Kom was stored for approximately six months in a roofed open-air storage building and then stored for two months in the laboratory. The materials were smashed into pieces using a hammer mill with 5 mm screen size and then sieved to obtain the fractions; the sieve sizes 5, 2.5, 1.25, 0.63, and 0.16 mm were used. Moreover, rubbed material was selected for comparison with the smashed material

2.2 METHODS

Table1. Process parameters and physical property indexes of observing sample

Sample	Particle size mm	Moisture content %	Pressure MPa	Temperature ℃	Density g · cm^3	Durability %	Compressive strength MPa	Shear strength MPa
1	＜0.16	11	90	110	1.157	98.96	62.12	6.77
2	Rubbed material	11	90	110	0.784	99.70	101.94	9.16
3	0.16-0.63	8	50	90	0.964	94.50	82.24	8.45
4	2.5-5.0	8	50	90	0.774	70.37	135.75	7.80
5	1.25-2.5	5	90	110	0.941	90.88	94.69	9.04
6	1.25-2.5	17	90	110	0.614	62.47	104.99	8.91
7	1.25-2.5	11	90	110	0.841	93.33	99.29	8.93
8	0.16-0.63	30	50	90	0.597	60.76	—	—

Note: “—”indicate the index is not measured.

The raw material is compressed using a stainless steel piston cylinder compression device with a single shaft and an inner diameter of 40 mm. The samples were divided into two sets. The first set of samples was densified briquettes which were cut with a slice knife, forming a cross section and a vertical section, and the bonding mechanisms were analyzed. The second set of samples was the fracture samples after compressive strength or shear strength test, which were used to analyze the failure mechanism.

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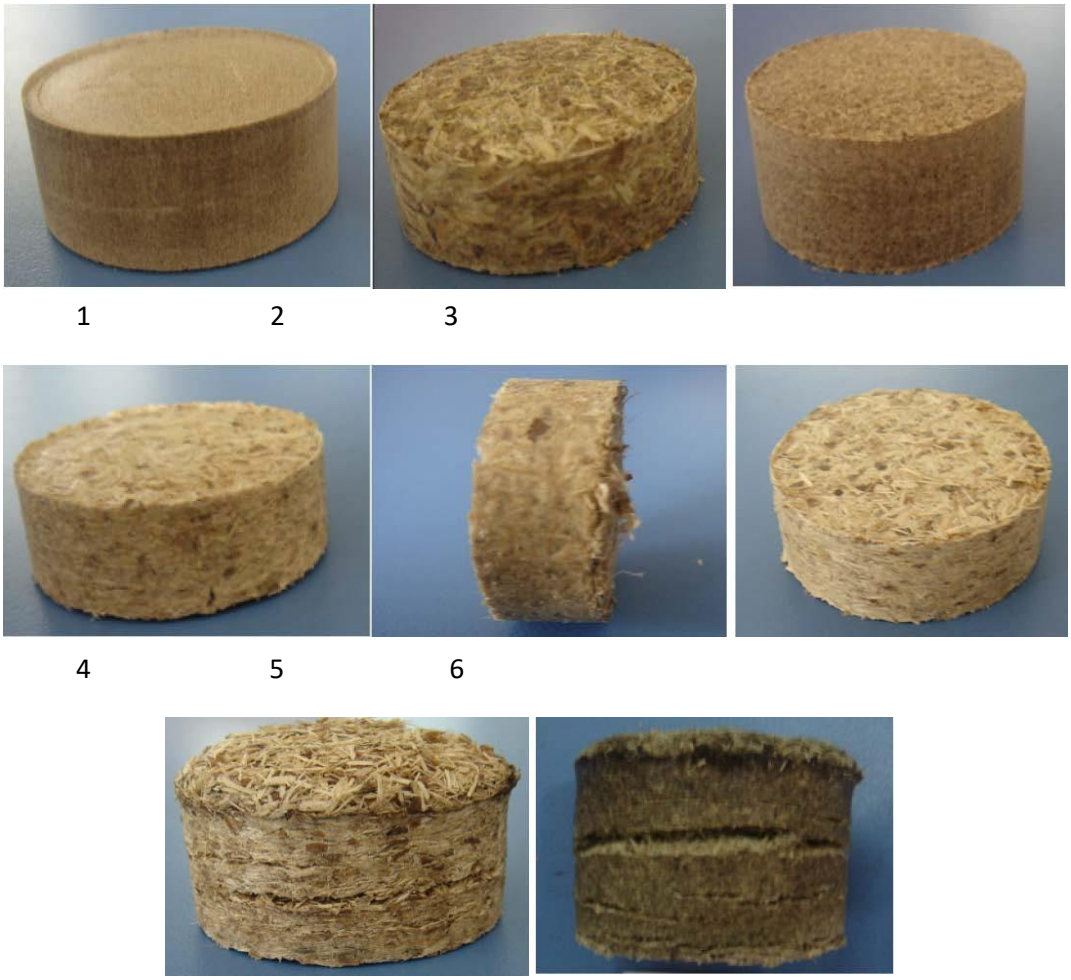

1 2 3

4 5 6

The specific operation method of physical properties of the briquettes(except the shear strength)was detailed in reference 1 [1], the results and samples were shown in Table 1 and Fig. 1, respectively. The shear strength of briquette was bilateral shear device was shown in Fig.2, and actual length of cut edge was 38.2 mm. It is defined as:

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shear device was shown in Fig.2, and actual length of cut edge was 38.2 mm. It is defined as:

$$\tau = \frac{F_x}{A} = \frac{F_x}{2 \times \frac{\pi}{4}\left(38.2 \times 10^{-3}\right)^2}$$

Where τ is the shear strength(MPa), A is the cross sectional area（m^2）, F_x is the value of the maximum load during deformation（N）, 38.2 is the actual length of cut edge（mm）.

2.3 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) (Hitachi S3400N) images of all samples were taken for fractured surfaces of the briquettes madein the laboratory and used to study the bonding mechanism and failure mechanism. To prepare the samples for taking of SEM images, the samples were mounted on astub and sputter coated with gold. The SEM observation conditions were at acceleration voltages of 5 kV and a distance of 10 mm. SEM observations were made at a magnification of 50×, 300 ×, and 800 ×. The SEM images were taken about two month after making the briquettes, which were stored in Zip-lock plastic bags at room temperature until used for imaging.

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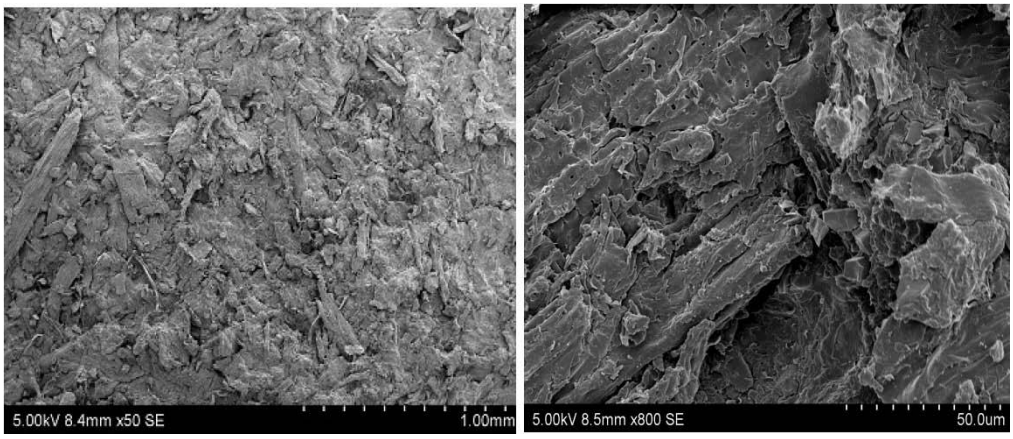
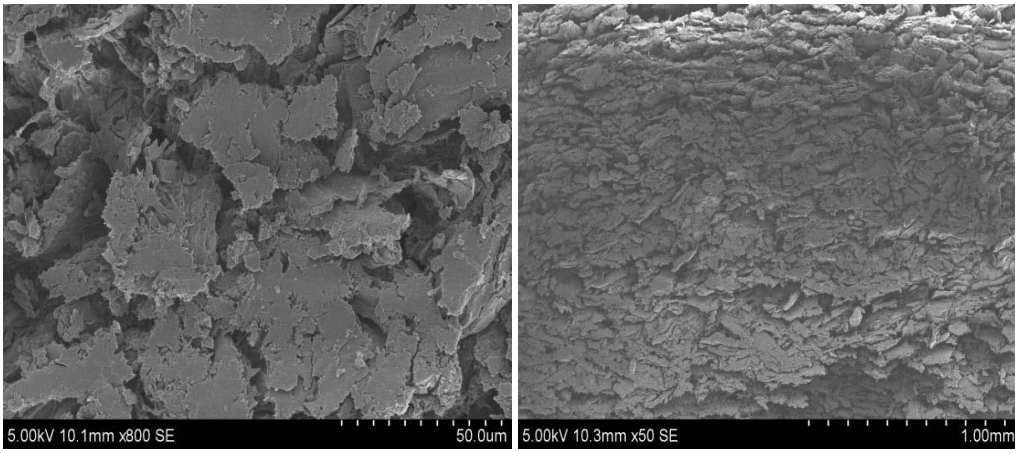


a Cross section



b Vertical section

Particle size: ＜0.16mm, Temperature:110℃,Pressure:90MPa, Moisture content:11% w.b

Fig.3 Scanning Electron Microscopy images（test 1）

3 RESULTS AND DISCUSSIONS

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3.1 Analysis of the adhesion mechanism test results

All samples belong to the first set.

The electron microscope photograph of the cross section of sample 1 (Fig. 3a) shows that only a few gaps are observed between the particles at any magnification, indicating that the particles bond are strong enough because of the filling of gap between the fine particles. When the distance between the particles is close enough, short-range force (such as hydrogen bonding, van der Waals' force and magnetic interaction) or molecular forces resulted in the strong bonding between adjacent particles and constituted solid bridge bonding between particles. As a result, the density of 0.16 mm sample is the highest in all samples. As can be seen from the photos (Fig. 3b) of the longitudinal section that there are many gaps between particles resulted from the compression inter-particles in the form of flake structure. Thus, the bonding is strong on the cross section of the fine particles, whereas, the bonding is weak on the longitudinal section. It can be concluded that the finer the particle size, the easier the filling between the particles, the higher the density and durability of the briquettes, this is probably due to that the fine particle was beneficial to the filling of gaps. Whereas, the bonding caused by short-range forces is weak and cannot resist the disruptive forces developed by elastic recovery following compression, resulting in the compressive strength and shear strength of fine particles were lower than larger particles.

The SEM images of the cross sections of the sample 2, i.e., briquette made from rubbed material (Fig.4a and Fig.4b)shows that there are larger gaps and obviously mechanical interlocking bonds in the cross section ata magnification of 50×, there are filler in the interlocking area ata magnification of 800×, resulting in the high density, high durability, and relatively high compressing strength and shear strength. This is probably because flat-shaped or silk-shaped materials interlocked or folded each other resulting in interlocking bonds which could resist the disruptive forces caused by elastic recovery during the compression process. Thus, the density(0.784 g · cm^{-3}) of the sample 2(rubbed material)is lower than the sample 1(＜0.16 mm) sample(1.157 g · cm^{-3}), the durability (99.70%) is almost equal to sample 1(98.96%), but the compressive strength (101.94 MPa)and shear strength (9.16 MPa)are higher than62.12MPaand 6.77 MPa of sample 1 under the same forming conditions.

Table 1 shows that under the same forming condition, the density and durability of the briquette (sample 4) with large particles (2.5-5.0 mm) are lower than those of the raw materials (sample 3) with fine particles (0.16-0.63 mm), and the compressive strength of the former is higher than that of the latter. Although the shear strength is not very different, all the physical properties are larger than that of the fuel with 0.16 mm particle size. As seen in Fig. 5a and Fig. 5b, there are more pore spacein the probably because flat-shaped or silk-shaped materials interlocked or folded each other resulting in interlocking bonds which could resist the disruptive forces caused by elastic recovery during the compression process. Thus, the density(0.784 g · cm-3) of the sample 2(rubbed material)is lower than the sample 1(＜0.16 mm) sample(1.157 g · cm-3), the

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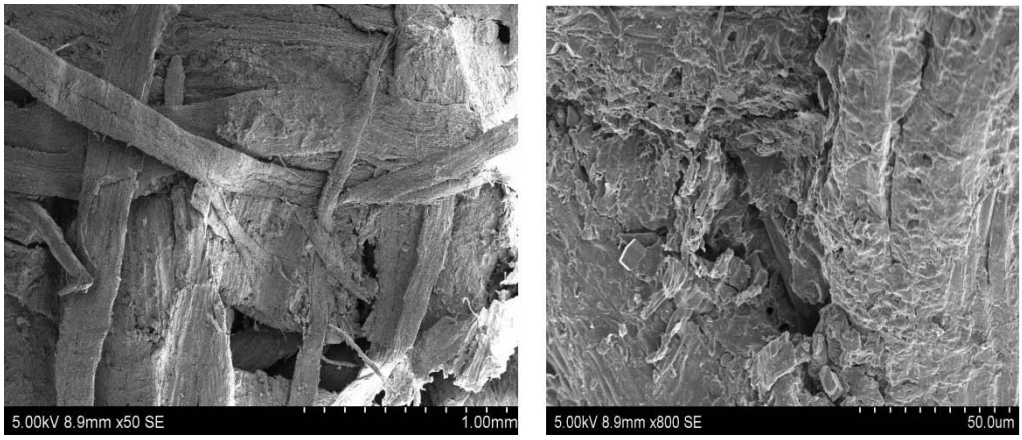

a 50× b 800×

rubbed material, Temperature:110℃, Pressure:90MPa, Moisture content:11% w.b

Fig.4 Scanning Electron Microscopy images of cross-section (test 2)

Table 1 shows that under the same forming condition, the density and durability of the briquette (sample 4) with large particles (2.5-5.0 mm) are lower than those of the raw materials (sample 3) with fine particles (0.16-0.63 mm), and the compressive strength of the former is higher than that of the latter. Although the shear strength is not very different, all the physical properties are larger than that of the fuel with 0.16 mm particle size. As seen in Fig. 5a and Fig. 5b, there are more pore spacein the sample 4 (2.5-5 mm) than the sample 3 (0.16-0.63 mm), resulting in an increase in the air volume between the particles; thus, the density and durability of the former are relatively lower than the latter.

Under the same conditions of particle size, temperature and pressure, compared with the sample with a moisture content of 8%, the density and durability of the sample 8 with a moisture content of 30% decreased from 0.964 g · cm-3 to 0.597 g · cm-3 and from 94.50% to 60.76% (Table 1), respectively. Fig. 5a and Fig. 5c show that there is a larger gap in its cross section, which may be caused by the water vapor that formed in the fuel with high moisture content at high temperatures

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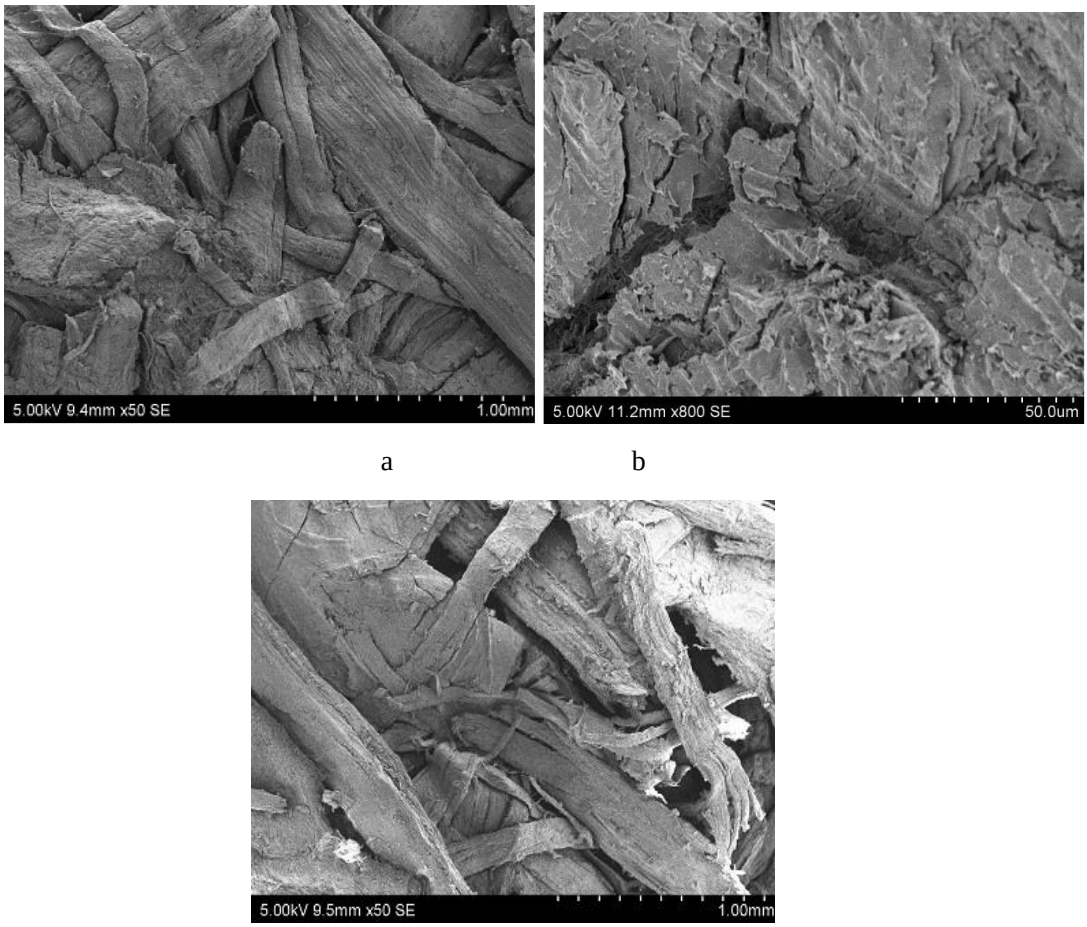

a b

c

a Particle size: 1.25~2.5mm, Temperature:110℃,Pressure:90MPa,Moisture content:5% w.b （50×）

b Particle size: 1.25~2.5mm, Temperature:110℃,Pressure:90MPa,Moisture content:5% w.b （800×）

c Particle size: 1.25~2.5mm, Temperature:110℃,Pressure:90MPa,Moisture content:17% w.b （50×）

Fig.6 Scanning Electron Microscopy images of cross-section (test 5、6)

The water vapor that is not discharged timely from the closed type of piston condenses into water between particles, forming a thicker layer of water film around the particle; the non-

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compressibility of water increases the gaps and hindered the bonding between particles, resulting in the decrease of density of the sample.

Water is considered the most effective substitute for binder and lubricant. As a thin-film binder, water can increase the contact area between particles and enable formation of van der Waals interactions, which improves adhesion. The film water around the particles results in binding through capillary adsorption between particles [5]. At a certain temperature, water can cause a wide range of physical and chemical reactions, such as thermal softening of biomass, denaturation of proteins, gelatinization of starch, and dissolution and continuous recrystallized of sugar and salt [11]. The research of Pickard showed that the degree of adhesion of alfalfa increased with an increased water content. The reason for this phenomenon is that the stem and leaf dipped in water will become softer, which is conducive to squeezing out proteins and other substances from the cell [12]. As seen in Fig. 6b, obvious cracks appear on the section of the whole particle with a moisture percentage of 5%. It is judged that brittle fracture occurs inside the particle, showing that water in the formation of particles is not sufficient and resulting in the great brittleness of the particles. Therefore, too much or too little water will cause adverse effects on the formation of biomass fuels.

The compressive strength of the fuel increased with increases in the moisture content (Table 1). For raw materials with a particle size of 1.25 ~ 2.5 mm, when the moisture content increased from 5% (sample 5) to 17% (sample 6), the compressive strength increased from 94.69 MPa to 104.99 MPa; however, the difference between the shear strengths is not large. Contrasting Fig. 6a and Fig. 6b, the structure of sample 5 is found to be denser than the sample 6, possibly because the fuel is formed in a closed structure. Excessive water vapor formed at a high temperature cannot be eliminated in a timely manner, and it continues to exist in the particles or re-condenses into water. The former case can activate the natural binder in the material, thereby promoting gelatinization of the starch and denaturation of the protein. For the latter case, a thicker water film is formed around the particle, forming bonding interactions between particles through capillary adsorption. In addition, the non-compressibility of water increases the gap between the particles. However, the effect of the latter is relatively small, which therefore leads to strong bonding between the particles. Greater external force is required to disrupt this bonding and fracture the fuel. The larger compressive strength and shear strength of the fuel are shown.

3.2 Analysis of the failure mechanism

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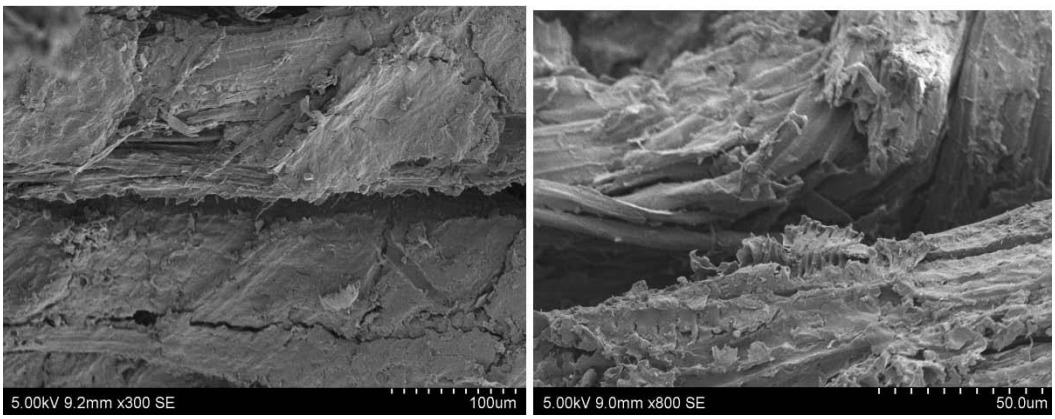

a （300×） b （800×）

Particle size: 1.25~2.5mm, Temperature:110℃, Pressure:90MPa, Moisture content: 11% w.b

Fig.7 Scanning Electron Microscopy images of cross-section (test 7)

In this experiment, the samples of complete sections after the tests of compressive strength and shear strength which belong to the second set are studied and analyzed.

Fig. 7 shows that an obvious crack is observed in the sample 7(1.25 ~ 2.5 mm). This crack is caused by the weak bonding between the particles and the rebound effect of the material and shows that the plastic flow of the non-crystalline polymer between particles is very small. No flat area was observed on the fiber surface, with the ends of the fibers and particles protruding from the surface. This is the result of tearing the adhesive structure and shows that the high energy is absorbed by the good bonding between the particles. The interface failure of a solid bridge is demonstrated, proving that the bonding mode is solid bridge caused by the nature binder and the binding strength of the binder is sufficiently high. The components of Caragana korshinskii Kom are cellulose (37.71% d.b.), hemicellulose (8.31% d.b.) and lignin (27.03% d.b.)[1]. The natural binders can be activated by the presence of moisture and high temperature and be squeezed out of the biomass cells because of the application of high pressures, which made solid bridges between the particles. These solid bridges will harden after cooling; this will cause the briquettes to become strong and durable [13]. The high-quality briquettes are possibly due to the fact that Caragana korshinskii Kom has a significant amount of lignin that possibly can soften and

In Fig. 1a, the fiber surface of sample 1(<0.16 mm) is flat, and a very small amount of particle detachment and no torn fiber ends are observed in the section, indicating that the adhesive structure is not torn and destruction occurs only in the inner layer of the binder. Cohesive failure occurred, demonstrating that the strength of the binder is not highenough.

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In this test, apparent interface failure and cohesive failure were observed only in the experimental section. Other damage forms may not appear separately. Even if they appear at the same time, it is not easy to distinguish among them. The failure mechanism of the fuel remains to be studied further.

4 CONCLUSIONS

The micro-structural analyses(scanning electron microscopy) of Caragana korshinskii Kom briquettes showed that the bonding in fine particles caused by short-range forces such as molecular force (valence force, i.e., chemical bonding, hydrogen bonding, and van der Waals force), electrostatic force and magnetic force can cause the solid particles to adhere to each other and the increase of density of briquette, which can't resist the disruptive forces produced by elastic recovery following compression and shear. The natural binders in the raw material and mechanical interlocking in the fibers, flat shaped particles and bulky particles created "solid bridge" type bonding between particles in the briquette, the lignin is the role binder which shapes the solid bridge inter-particle. Activating the natural binder through appropriate moisture and high temperature in the range of glass transition is essential to produce high quality briquettes.

Furthermore, the interface failure of solid bridge appeared in bulky particles, the cohesive failure appeared in the fine particles. It is not easy to distinguish all failure mechanism types.

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