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Co-pelletization of sewage sludge and biomass: The density and hardness of pellet

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HIGHLIGHTS

- Co-pelletization of sludge and biomass was investigated.
- Effect of process parameters on pellet properties was examined.
- The mechanisms of inter-particular adhesion bonding were studied.
- Higher quality pellets can be produced at lower pressure and temperature.
- Synergies of protein and lignin could be the mechanism of the co-pelletization.

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ABSTRACT

In the present study, the effects of process parameters on pellet properties were investigated for the co-pelletization of sludge and biomass materials. The relaxed pellet density and Meyer hardness of pellets were identified. Scanning electron microscopy, FT-IR spectra and chemical analysis were conducted to investigate the mechanisms of inter-particular adhesion bonding. Thermogravimetric analysis was applied to investigate the combustion characteristics. Results showed that the pellet density was increased with the parameters increasing, such as pressure, sludge ratio and temperature. High hardness pellets could be obtained at low pressure, temperature and biomass size. The optimal moisture content for co-pelletization was 10–15%. Moreover, the addition of sludge can reduce the diversity of pellet hardness caused by the heterogeneity of biomass. Increasing ratio of sludge in the pellet would slow down the release of volatile. Synergistic effects of protein and lignin can be the mechanism in the co-pelletization of sludge and biomass.

1. Introduction

Besides wind and solar energy, bio-energy is one of the widely employed renewable energy technologies (Chen et al., 2011). Bio-energy includes various natural and derived materials primarily categorized as agricultural residues, forest lopping wastes, animal dung and municipal sludge, etc. Biomass has become a valuable renewable energy resource due to its attractive properties, such as low production cost, low acidic gas emissions and no net carbon dioxide (Chou et al., 2009). Moreover, it plays an important role in reducing the import of fossil fuels. Therefore, the research of bio-energy has attracted widespread attention.

Sewage sludge (SS) is a large volume byproduct of the municipal wastewater treatment plants. The treatment and disposal of SS have been one of the most severe environmental problems in China. About 20.76 million tons of SS containing 80% moisture content has been generated in 2010 (Zhao et al., 2013). Furthermore, this amount is expected to increase at the end of 2015 on the basis of the China's 12th Five-Year Construction Plan for National Urban Wastewater Treatment and Recycling Facilities (Zhao et al., 2013). In addition, SS carries many hazardous substances such as heavy metals, synthetic organic compounds, dioxins, and pathogenic

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microorganisms (Manara and Zabaniotou, 2012), making it difficult to dispose. However, SS also contains a large amount of organic compounds which are principally proteins and carbohydrates.

Currently, refuse-derived fuel (RDF) technology has become a popular refuse fuel processing technology that is widely applied in developed countries (Chen et al., 2011; Prawisudha et al., 2012), as it is cost effective and environment friendly. The prime merits of RDF are its size, low level of pollution, high and constant heating value, and that it does not emit a stink. Furthermore, as it is shrank to one-tenth of its original size after extruding, it can enhance the utilization of biomass fuels from the standpoints of storage, transportation and logistic handling (Chen et al., 2011; Marsh et al., 2007). The sludge RDF, in the form of pellets or briquettes, can be stored safely without the risk of secondary environmental pollution. And the area of their potential outlets is expanded as they can be transported easily (Wzorek, 2012).

In order to improve the combustion characteristics of SS, the most popular method is to mix the sludge with auxiliary fuel (coal, refuse, sawdust, etc.), desulfurizer and binder to produce solid fuel. In 1998, Dospoy et al. (1998) firstly managed to produce sludge derived fuel from paper sludge, powder coal, and plastics and applied them in the market. Nowadays, several studies have been conducted, focusing on the physical properties and combustion characteristics of sludge RDF. Chen et al. (2011) investigated the characteristics of a sludge RDF and the combustion behaviors. It was concluded that the usage of organic sludge as an alternative fuel was cost effective and had environmental benefits. Zhao et al. (2013) developed an RDF technology, including the steam explosion pretreatment, mechanical dewatering, natural drying and pelleting, to produce solid fuel from SS. Wzorek (2012) studied the physical and chemical properties and the calorific values of three types of sludge-derived fuels, then applied them to the cement clinker manufacturing process. In biomass pelleting manufacturer, many reports have been focused on the mechanisms of process parameters(i.e., pressure, temperature, moisture content, particle size) on pellet quality (Kaliyan and Morey, 2010; Carone et al., 2011). However, little information is available on the effects of these parameters on pelletization process of sludge RDF.

In this study, three different raw materials (Chinese fir, camphor and rice straw) were mixed with SS for pelletization, representing softwood, hardwood and herb, respectively. The preparation of co-pelletization pellets was described and their relaxed pellet density and Meyer hardness were characterized. The effects of pressure, die temperature, moisture content, sludge ratio and biomass size on the pellet properties were also investigated. The combustion characteristics of pellets were subjected to thermogravimetric analysis under an oxidizing atmosphere. The main purpose of this study was to illuminate the mechanisms of pelletization by scanning electron microscope, infrared spectroscopy and chemical component analysis.

2. Methods

2.1. Materials

The dewatered sewage sludge and three different biomass materials were used as the raw material in the study. The sludge was obtained from an urban sewage plant in Changsha city, Southern China. The biomass materials were Chinese fir (*Cunninghamia lanceolata* (Lamb.) Hook.), camphor (*Cinnamomum camphora* (L.) J. Presl), and rice straw (*Oryza sativa* L.), representing the class of softwoods, hardwood and grass, respectively. All of the feedstocks were air-dried and then put in an oven at 40 °C for 48 h. The dried materials were pulverized in a rotary cutting mill and then screened into fractions of particle diameter less than 0.45 mm except for biomass size experiment. The final dried samples were stored in a desiccator at room temperature. The ultimate and proximate analysis results and some physicochemical parameters of the samples above are shown in Table 1.

The ground samples were dried in a convection oven set at 40 °C before pelletization. The moisture content of samples was adjusted by adding predetermined amounts of deionized water onto the particles and stored at 4 °C for 48 h to enable moisture to be distributed uniformly. Sludge sample and biomass samples were weighed and mixed manually to produce the required blends. The percentage of the blends was calculated on a dry weight basis. The mixed samples were kept in a sealed plastic container at 4 °C until pelletization.

2.2. Physicochemical analysis

The element compositions of the raw materials were analyzed by CHNOS Elemental Analyzer Vario EL III (Elementar Analysen systeme GmbH, Germany). Proximate analysis was carried out according to the Standard Practice for the Proximate Analysis of solid biofuels (GB/T28731-2012) using a Jinghong SXL-1002 program control chamber electric furnace (China). The higher heating value (HHV) was determined using an oxygen bomb calorimeter (SUNDY SDACM5000, China) from three replicates. The amounts of cellulose, hemicellulose and lignin were obtained using Van Soest detergent fiber analysis by automated fiber extraction analyzer (Gerhardt fibretherm FT12, Germany). Protein was calculated by multiplying the concentration of organic nitrogen by 6.25 reported by Shao et al. (2013).

2.3. Pelletization and characterization of the pellet

The pellets in this work were prepared using a single pellet press unit which allowed simulation of the pelletizing process in a press channel of a pellet mill (Lam et al., 2012). More details about pelletization unit and the test procedure can be found in our previous researches (Li et al., 2012; Wang et al., 2013).

For the present study, the hole in the cylinder was filled with approximately 1.0 g of mixed raw materials accordance with a predetermined ratio to make a single pellet with 7.5 mm in diameter and 20 mm in length. The effects of pressure (28–110 MPa), die temperature (30–150 °C), moisture content (5–25%), sludge

Table 1
Properties of raw sewage sludge and biomass samples.

Analysis	Sewage sludge	Chinese fir	Camphor	Rice straw
Proximate analysis (wt.%)				
Moisture	5.42	7.63	6.67	6.56
Volatile matter	57.22	74.49	79.02	64.59
Fixed carbon	6.09	16.68	12.53	13.51
Ash	31.27	1.20	1.78	15.34
Ultimate analysis (wt.%)				
C	36.11	49.08	48.18	45.04
H	5.25	5.96	6.09	5.05
N	6.50	0.63	0.70	1.06
S	1.03	0	0	0
O[a]	51.11	44.33	45.03	48.85
Chemical analysis (wt.%)				
Protein	35.50	–[b]	–[b]	–[b]
Hemicellulose	–[b]	12.05	20.82	24.60
Cellulose	–[b]	36.22	38.87	41.33
Lignin	–[b]	27.61	24.40	9.22
HHV (MJ/kg)	15.59	18.38	18.40	14.64

[a] By difference.
[b] Not measure.

ratio (20–100%) and biomass size (0.2–0.85 mm) on the pellet quality were investigated.

The effects of pelletization conditions on the quality of pellets were evaluated in terms of pellet density and Meyer hardness. The relaxed pellet density was based on measured mass, length, and diameter of individual pellet after storing inside a sealed plastic bottle at 4 °C for two weeks.

Hardness is one of the important properties of commercial pellets, which reflects the mechanical strength of single pellet during handling, transportation, and storage. In this study, the Meyer hardness of pellets was analyzed in the same single pellet press unit with a hemisphere-end rod. Compressive force was applied to the center of the cylindrical pellets after placed horizontally on a steel plate. The tester was run at a speed of 2 mm/min and stopped after the pellet was fractured. The maximum load to break the pellet was recorded. The Meyer hardness, H_m, defined as the applied force divided by the projected indentation area and was calculated by the following equation (Lam et al., 2011).

$$H_m = \frac{F}{[\pi(Dh - h^2)]} \quad (1)$$

where h is the indentation depth (mm); F is the maximum force when the pellet is broken (N); and D is the diameter of rod (mm).

Combustion characterization of the pellets was carried out by thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) using a thermobalance TGA-7300 (Japan). TGA is one of the most useful techniques available for rapidly investigating combustion characteristics of solid fuel (Chandrasekaran and Hopke, 2012; Gil et al., 2010). All combustion experiments were conducted with a heating rate of 15 °C/min from room temperature to 850 °C under an air flux of 100 mL/min. Approximately 6 mg of sample was used for each experiment.

2.4. SEM and FT-IR analysis

The bonding mechanism of the pellets was studied using a scanning electron microscopy (SEM) (FEI QUANTA-200, Holland FEI Company, Holland) by fracture surface analysis. In order to analyze the functional groups changes during temperature increasing, FT-IR spectra of the pellet surface were recorded using a FT-IR spectrophotometer (WQF-410, Beijing, China). The dry ground sample (about 0.1 g) was mixed with KBr (0.1 g) and pressed into a tablet, which was then analyzed by an infrared spectrometer.

3. Results and discussion

3.1. Effect of pressure

The effect of pressure on pellet density and Meyer hardness in the co-pelletization of sludge and three biomass materials is shown in Fig. 1. In this study, the pressure applied was 28, 41, 55, 69, 83, and 110 MPa when temperature, sludge ratio, moisture content were controlled at 90 °C, 50% and 15%, respectively.

The density of pellets was an important factor relating to the handling and transporting of RDF pellets. As shown in Fig. 1a, the relaxed pellet density increased continuously with increasing pressure. It increased from 962.7 to 1070.6 kg/m^3 for Chinese fir and SS pellet (CFSP), from 943.3 to 1042.6 kg/m^3 for camphor and SS pellet (CSP), and from 1051.3 to 1151.3 kg/m^3 for rice straw and SS pellet (RSSP), respectively. Moreover, a similar trend of three different pellets was found through the polynomial fitting shown in Fig. 1a. Sludge particles can be squeezed into the gaps and voids of biomass particles, and then protein denaturation and lignin softening serve as the binders under high pressure. This can reduce the number of empty spaces between particles. It is

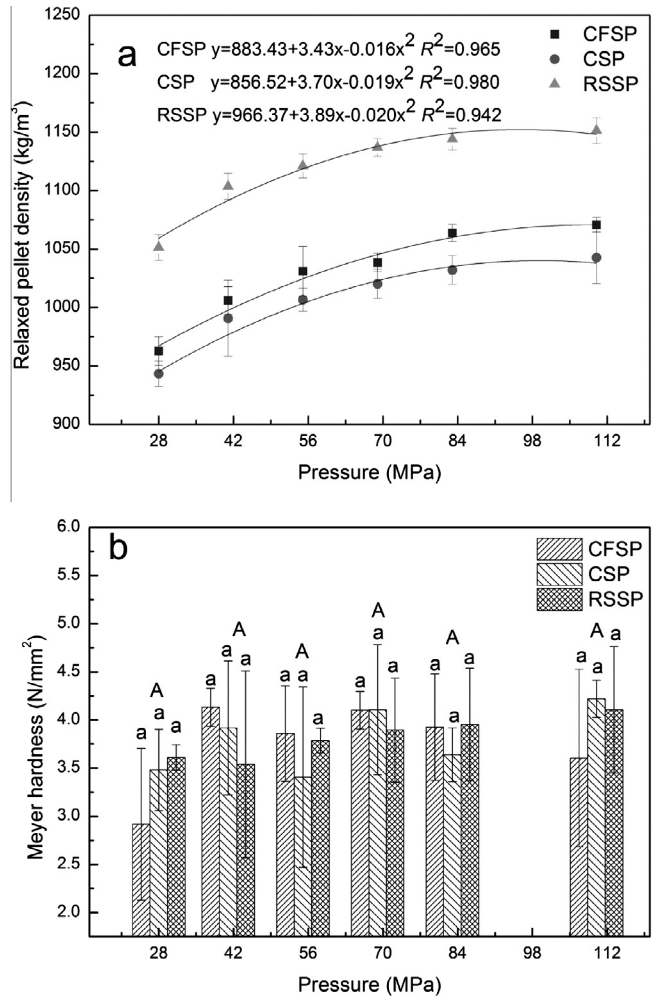

Fig. 1. Effect of pressure on relaxed pellet density (a) and Meyer hardness (b) of pellets. Bar groups with different capital letters indicate a significant difference ($P < 0.05$) between different pressures applied. Bars with different lowercase letters indicate a significant difference ($P < 0.05$) among three biomass materials under the same pressure.

responsible for the increase of the pellet density with increasing pressure.

In wood pelletization industry, pressure is a significant factor for pellet compressing. It is a commonly industrial technique to promote adhesion by increasing molecular contact between adjacent molecules. The higher the pressure, the closer the solid particles are, resulting in the higher pellet density. Previous research showed that the pellet density increased exponentially with the applied pressure during densification of palm fiber and shell (Husain et al., 2002). However, the production of higher density pellets has less dependence on the pressure in this study. In other words, higher density pellets can be prepared under low applied pressure.

In addition, RSSP always has the higher relaxed pellet density than CSP and CFSP under the same conditions (Fig. 1a). Three reasons may be contributed to that result. First, RSSP have a relatively higher weight but smaller size observed in this experiment. Second, the expansion ratio of RSSP (0.42–0.83%) is much lower than that of CFSP (0.99–2.12%) and CSP (0.69–1.71%), which is measured after being stored in the freezer at 4 °C for two weeks. The lower expansion ratio of RSSP indicates a good viscosity which may be caused by the low lignin glass transition temperature (T_g) of straw (Stelte et al., 2011a). Third, the higher pellet density of RSSP can be ascribed to the presence of the silica in the SS and rice straw (Liu et al., 2014), and this explanation is consistent with high ash content as revealed by the proximate analysis (Table 1).

Chinese fir particles are thin strips while camphor particles are square block. Thin strips can form more structural gaps which would be filled with sludge particles to be more compact structure. Camphor has a higher content of hemicellulose and cellulose than fir, which is 59.69% and 48.27%, respectively. Hemicellulose and cellulose may entangle and fold between particles. Due to their resilience characteristics (e.g., elasticity and stiffness), hemicellulose and cellulose may not make good bonding between particles. The difference of material particle shape and fiber content may be the reasons for the higher density of CFSP than CSP.

Under higher pressure, particles were brought close together causing inter-particle bonding. The natural binding components such as starch, protein, lignin, and water soluble carbohydrate in the SS and biomass materials are squeezed out of the particles, which contributing to make solid bridges (Kaliyan and Morey, 2010). All of those are beneficial to form the stronger solid bridges and short-range forces (i.e. hydrogen bondings, van der Waals' forces, and electrostatic forces). So theoretically, the higher the pressure applied, the larger hardness value obtained.

While no significant correlation between pressure and Meyer hardness was observed by one-way analysis of variance in this experiment (Fig. 1b). Meanwhile, the differences between biomass materials are also non-significant (Fig. 1b). These results implied that the addition of sludge could significantly reduce the dependence on pressure for producing high hardness pellets. Moreover, it can reduce the hardness diversity caused by the heterogeneity of different biomass feedstocks in the pelleting industry. Synergistic effects of sludge and biomass can be used to explain the above phenomenon. First, sludge particles fill in the gaps and voids between adjacent biomass particles. After then, protein will plasticize under heat and act as a binder. Meanwhile, lignin will soften and diffuse from one particle to another at the points of contact to form solid bridge. The applied pressure is associated with production costs and pellet quality. As a result, it is significant to obtain pellets with high density and hardness under low pressure applied.

3.2. Effect of sludge ratio

The effect of sludge ratio on pellet density and Meyer hardness was studied at 55 MPa, 90 °C and 15% moisture content (Fig. 2). The relaxed pellet density increased with increasing sludge ratio. For instance, it was improved from 851.2 to 1270.3 kg/m^3 for CFSP when the sludge ratio was increased in the range of 20–80%. Moreover, there is a good linear relationship between relaxed pellet density and sludge ratio, with regression coefficients (R^2) of 0.994, 0.999 and 0.992 for CFSP, CSP and RSSP, respectively. It was indicated that the physical and chemical properties of the sludge had a decisive influence on the pellet density.

As shown in Fig. 2b, the hardness of CFSP and CSP increased remarkably with the hardness of RSSP increase. It can be confirmed from the slope of the linear fitting between hardness and sludge ratio (Fig. 2b). The slope of RSSP line is 0.026, lower than that of CFSP (0.037) and CSP (0.037). Via linear fitting, a good linear relationship was found between the Meyer hardness and sludge ratio. At significance level $\alpha = 0.01$, the linear relationship is significant ($R^2 > 0.841$, $n = 6$, $\alpha = 0.01$). The lower hardness of pellet was obtained at lower sludge ratio, indicating that the existence of pore spaces and gaps in the pellet reduced the pellet resistance to deformation. This was confirmed by comparing the CFSP made at 20% and 80% sludge ratio through cross section SEM micrographs (Fig. S1a, S1b in Supplementary data), in which clear gaps and spaces were identified in the lower sludge ratio pellet. During the hardness test, the presence of spaces and gaps promoted the relative movement of particles within the pellet matrix, resulting in the lower hardness for the CFSP made at 20% sludge ratio (Li et al., 2012).

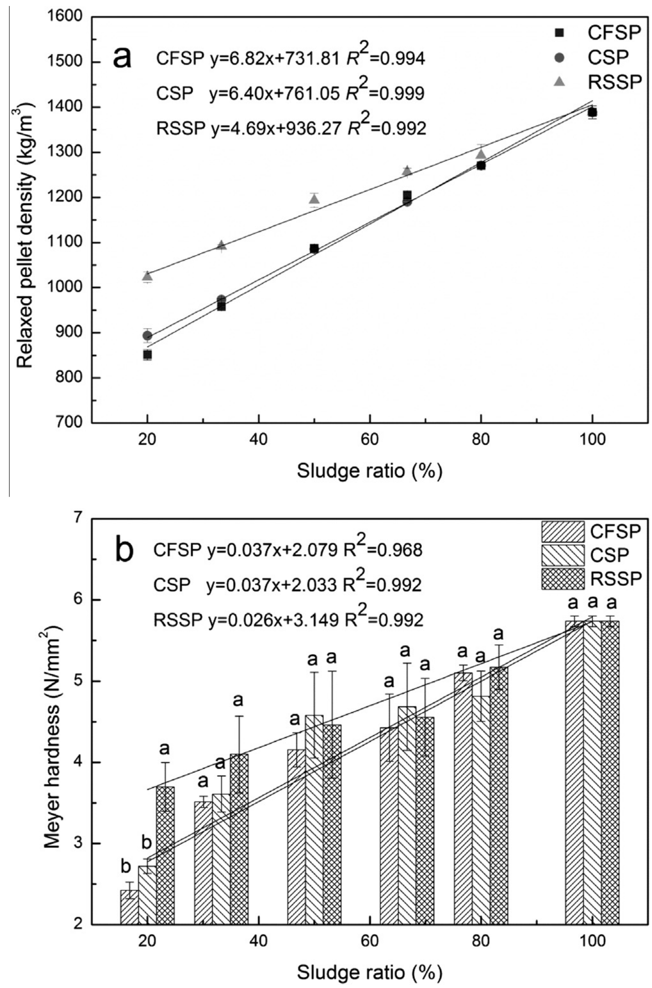

Fig. 2. Effect of sludge ratio on relaxed pellet density (a) and Meyer hardness (b) of pellets. Bar groups with different capital letters indicate a significant difference ($P < 0.05$) between different sludge ratios. Bars with different lowercase letters indicate a significant difference ($P < 0.05$) among three biomass materials under the same sludge ratio.

The natural binders that were coated on the particles in the pellets were primarily lignin and protein compounds (Kaliyan and Morey, 2010). Through the above analysis, both density and hardness have a good linear relationship with sludge ratio for all pellets, which may indicate that the protein in the sludge could be the main binder in the co-pelletization of sludge and biomass at milder compression condition (<55 MPa and <90 °C). Protein denaturation temperature was above about 57 °C (Porter and Vollrath, 2012) while the mean lignin softening temperature was 75 °C with depends on species of biomass (Kaliyan and Morey, 2009a). This means that protein would denature and serve as the binder while lignin slightly softens. This may be the reason for the phenomenon that density and hardness have a good linear relationship with sludge ratio.

Table 1 shows that the protein content of SS is 35.50%, the lignin content of Chinese fir, camphor and rice straw were 27.61%, 24.40% and 9.22%, respectively. It is clear that the lignin contents of Chinese fir and camphor are approximate, but much higher than rice straw. Therefore, the synergistic effects of proteins and lignin in CFSP and CSP are more prominent, which is the potential cause for the higher slope of CFSP and CSP than RSSP.

In the case of the wood pellets, steam conditioning, pre-heating or additives were used to obtain higher strength pellets (Kaliyan and Morey, 2010; Tooyserkani et al., 2013). The addition of suitable binders and the usage of steam conditioning or pre-heating could improve the pellet strength. However, the costs of the plasticizer, the high energy consumption, combustion properties and environmental impacts have to be considered. In this study, the ratio of sludge exhibited a significant effect on pellet density and hardness, indicating that the sludge could be an appropriate binder for biomass pelleting.

3.3. Effect of die temperature

A comparison of the pellet quality at 55 MPa, 50% sludge content and 15% moisture content with different die temperatures is presented in Fig. 3. The relaxed pellet densities of CFSP and CSP increased initially when the die temperature increased in the range of 30–110 °C, and then decreased with further die temperature increasing. Moreover, it is clearly shown that the die temperature had little effect on the relaxed pellet density of RSSP from 70 °C to 150 °C.

As described in Section 3.2, the synergistic effects of protein denaturation and lignin softening are the main binding types in the co-pelletization of sludge and biomass. Protein denaturation usually occurs at temperatures above about 57 °C (Porter and Vollrath, 2012). The glass transition (i.e., softening) takes place from 50 °C to 113 °C for biomass materials. The mean T_g is 75 °C for the moisture content range of 10–20% (w.b) (Kaliyan and Morey, 2009a). The similar result has been reported by Uslu et al. (2008).

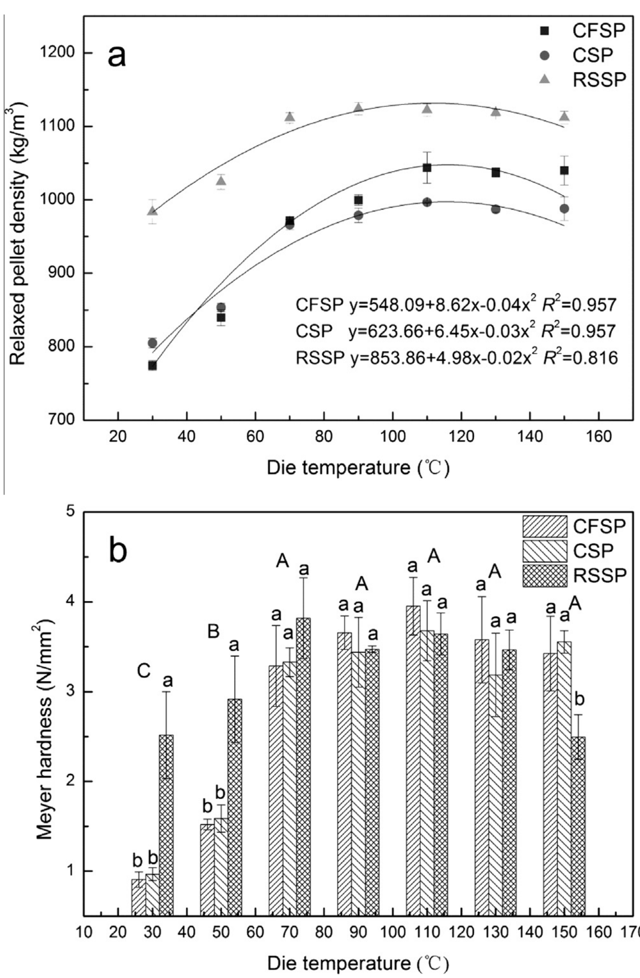

Fig. 3. Effect of die temperature on relaxed pellet density (a) and Meyer hardness (b) of pellets. Bar groups with different capital letters indicate a significant difference ($P < 0.05$) between different die temperatures. Bars with different lowercase letters indicate a significant difference ($P < 0.05$) among three biomass materials under the same temperature.

In the present study, the lignin and protein contained in raw material did not act as a binder at the low die temperature. Therefore, the bonding forces involved in the pellets are mainly related to short-range forces including hydrogen bridges, van der Waals force, free chemical bonds and mechanical interlocking. This binding mechanism explains the low pellet density at the 30 °C cases. As the temperature increased, lignin softened and protein denatured, after then bound the pellets upon compression. Once exiting the pelletizer, pellets were left to cool down, causing lignin hardened again and protein reassociated to enhance the pellet strength (Carone et al., 2011; Li et al., 2012). It is responsible for the much higher pellet density from 70 °C to 150 °C for those three kinds of pellets. On the other hand, because of the softening effect of temperature on lignin, an increasing temperature leads to lignocellulosic fibers plasticization. Therefore, the modulus of elasticity of particles becomes lower and the biomass becomes more flexible. It results in empty spaces between and within the particles reducing and the density of pellets increasing. Attention should be paid to the slight decrease of pellet density when the temperature over 110 °C. The possible reason is that the moisture had nearly all evaporated at 130 °C or 150 °C, and the liberation of water from the pellet has a negative impact on the quality of the pellets. Gilbert et al. (2009) has reported the similar result which showed a decrease of pellet density at 125 °C.

Similar to the effect of temperature on pellet density, the hardness tests shown in Fig. 3b further confirmed that lignin and protein were acting as the natural binders. It is depicted in the figure that the Meyer hardness increased when the temperature was lower than 70 °C and had no significant increase with further heat addition. It indicates that the die temperature needed for the co-pelletization of sludge and biomass is much lower than the wood pelletization which is above 100 °C. It is significant to reduce the production costs and energy.

Comparing the fracture surfaces of CFSP prepared at 70 °C with those prepared at 110 °C (Fig. S1 in Supplementary data), significant differences can be observed. First, the gaps and voids (Fig. S1c in Supplementary data) are an indication of poor adhesion between adjacent particles. Second, there is more interfacial contact area at 110 °C, possibly due to the fact that the presence of lignin and protein that possibly can soften or denature, and makes the particles more flexible at elevated temperatures. At the same time, lignin flow and inter-diffusion between adjacent wood particles, and protein fill into the gaps under pressure. After cooled down, solid bridges were formed between particles and fines, resulting in the increment of pellet hardness.

In the report of Stelte, the straw pellets had a lower compression strength compared with wood pellets as the presence of a chemical weak boundary layer caused by the wax in the straw (Stelte et al., 2011b). Attentions would be paid to the larger hardness value of RSSP compared with CFSP and CSP when the temperature below 70 °C. Furthermore, the hardness of three pellets have no significant difference from 70 °C to 130 °C. This indicates that the addition of sludge has a positive effect on straw pelleting especially under low temperature. The result in this study may be caused by the low T_g of protein which is the main binder discussed in Section 3.2 and the different softening temperature of three biomass lignin due to chemical differences. Softwood lignin has a higher Tg than hardwood and grass lignin due to the presence of more cross-links in softwood lignin caused by the absence of methoxy groups (Stelte et al., 2011a). This may be the reason for the little lower hardness for CFSP compared with CSP below 70 °C. Nevertheless, they have the higher values from 90 °C to 130 °C as the higher content of lignin for Chinese fir and enough heat for softening. Another interesting feature is that the hardness of RSSP is significant lower than CFSP and CSP at 150 °C. This suggests that protein would become brittle after excessive denaturation at high temperature and it could do harm to the pelletization. However, the higher lignin content of wood materials would offset this adverse effect, thus resulting in the relative high hardness.

The pellet surface was analyzed by ATR-FTIR spectroscopy for revealing the functional groups on the surface. Meanwhile, the difference between pellets pressed at 90 °C and 150 °C was indicated in Fig. S2 (in Supplementary data). The main spectral bands were 2928–2856 cm^{-1} (fatty acids), 1648–1643 cm^{-1} (amide I), 1550 cm^{-1} (amide II), 1510 cm^{-1} (lignin), 1455 cm^{-1} (methyl groups), 1243 cm^{-1} (amide III), 1110–1047 cm^{-1} (carbohydrates), 1030 cm^{-1} (cellulose component) and 900–600 cm^{-1} (fingerprint region), respectively (Stelte et al., 2011b; Zhu et al., 2012). The peaks at 2928 and 2856 cm^{-1}, which are attributed to aliphatic C–H group stretches caused by waxes and oils. As shown in Fig. S2 (in Supplementary data), the C–H absorption bands of RSSP is more intense than CFSP which can be explained by the fact that straw has a significant waxy layer. However, the presence of fat can result in lower pellet durability as higher levels of fat affect the binding functionality of lignin and protein (Kaliyan and Morey, 2009b). This is the possible reason for the lower hardness of RSSP relative to CFSP when the temperature over 90 °C (Fig. 3b).

3.4. Effect of moisture content

The effect of moisture content on the pellet characteristics is depicted in Fig. 4. The data was obtained from the experiments carried out at 55 MPa, 90 °C with sludge ratio of 50%. The relaxed pellet density increased initially with the moisture content increasing from 5% to 15%, and then decreased. The hardness of pellets demonstrated the similar trend, which peaked at the moisture content of 10%. Therefore, the appropriate moisture content for co-pelleting pellet was 10–15%. This result is consistent with previous studies which showed that density and durability (similar to hardness) of the densified products have a peak at optimum moisture content. Moisture content above or below this range would lead to lower quality pellets (Kaliyan and Morey, 2009b; Serrano et al., 2011).

Moisture in the pelleting process acts as both a binder and a lubricant. Water acts as a film type binder with hydrogen bonding by increasing the contact area of the particles. In addition, a thin film of water around the particles would exhibit bonds via capillary sorption between particles (Kaliyan and Morey, 2010). Water aids briquetting when water-soluble compounds are present in the feed such as starch, sugar, soda ash, sodium phosphate, potassium salt, and calcium chloride, etc. (Kaliyan and Morey, 2009b). After heating process, water induces a variety of physical and chemical changes such as denaturation of proteins, thermal softening of biomass, gelatinization of starch, and consecutive recrystallization of carbohydrates (Kaliyan and Morey, 2010). Therefore, a minimum amount of water is needed for the softening of lignin, the denaturation of proteins and developing capillary pressure and interfacial force (Carone et al., 2011). Fig. 4 clearly shows that the density and hardness of the pellets are poor for low moisture conditions.

In the present study, good quality pellets can't be produced at moisture content above 20%, because moisture trapped within the particles may prevent complete flattening and the release of natural binders from the particles due to the incompressibility of water (Kaliyan and Morey, 2009b). It is also possible that hydrogen bonds between polymers of particles are replaced by bonds to water molecule, resulting in forming water films between

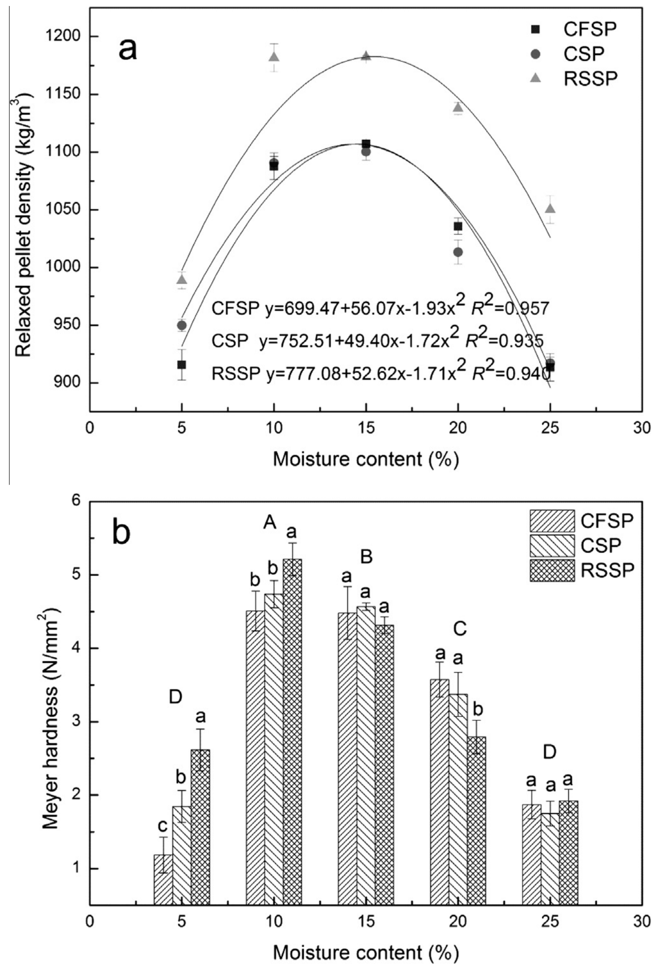

Fig. 4. Effect of moisture content on relaxed pellet density (a) and Meyer hardness (b) of pellets. Bar groups with different capital letters indicate a significant difference ($P < 0.05$) between different moisture contents. Bars with different lowercase letters indicate a significant difference ($P < 0.05$) among three biomass materials under the same moisture content.

particles. Water film causes a relative sliding between the particles, which may be the reason for pellets fracturing under high moisture content conditions observed in this study.

Meanwhile, the hardness of pellet at the moisture content of 5% runs is shown in Fig. 4b, which depicts that the hardness of pellets increases while the lignin content of biomass materials decreases. Two reasons may be contributed to it. First, the *Tg* of fir is higher than that of camphor and straw (Stelte et al., 2011a). Second, the lignin temperature would improve at the lower moisture condition (Kaliyan and Morey, 2010).

3.5. Effect of biomass size

The effect of biomass size on the pellet characteristics is shown in Fig. 5. This study was controlled in a common particle size reduction range (<0.20 mm, 0.20–0.30 mm, 0.30–0.45 mm, 0.45–0.85 mm and 0.85–1.18 mm) at 55 MPa, 90 °C and 15% moisture content. As depicted in Fig. 5a, the relaxed pellet density increased slowly with the decreasing biomass size, which was consistent with the report of Mani et al. (2006), Carone et al. (2011) and Shaw et al. (2009).

Biomass size is an important factor on pellet hardness. Several literatures reported an increase in durability of biomass pellet when reducing the biomass size (Mani et al., 2006; Carone et al., 2011; Shaw et al., 2009). As shown in Fig. 5b, the Meyer hardness

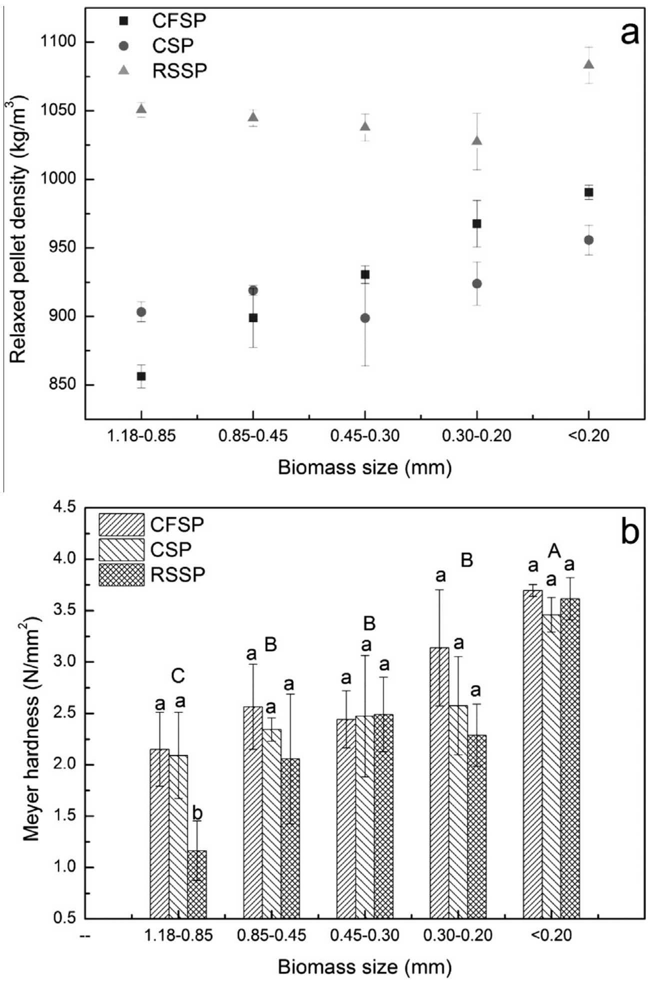

Fig. 5. Effect of biomass size on relaxed pellet density (a) and Meyer hardness (b) of pellets. Bar groups with different capital letters indicate a significant difference ($P < 0.05$) between different biomass size. Bars with different lowercase letters indicate a significant difference ($P < 0.05$) among three biomass materials under the same biomass size.

of pellets increased when the biomass size decreased. Furthermore, the experimental data show significant relevance ($P < 0.05$) between the biomass size and Meyer hardness (Fig. 5b) analyzed with one-way analysis of variance.

In this study, finely ground materials tend to give high density and hardness pellets. When reducing the biomass size, the small particles filled the empty spaces better by rearrangement. Moreover, finely ground biomass provides a greater surface area, thus facilitating the absorption of heat and moisture. It is significant to activate the binding properties of chemical components (e.g., protein and lignin) (Kaliyan and Morey, 2009b; Carone et al., 2011). Also, large particles are fissure points that cause cracks and fractures in pellets which can be found when biomass size above 0.45 mm in this experiment. Although fine particles can produce pellets with higher density and hardness, fine grinding is undesirable because of the increased cost of production.

3.6. Combustion characteristics

In order to evaluate the effect of the amount and the type of raw material (biomass and sludge) on the combustion characteristics, the pellets were subjected to thermogravimetric analysis under an oxidizing atmosphere. TG and DTG profiles depicting the combustion process of pellets are presented in Fig. 6. The characteristic combustion parameters of the pellets are summarized in Table 2.

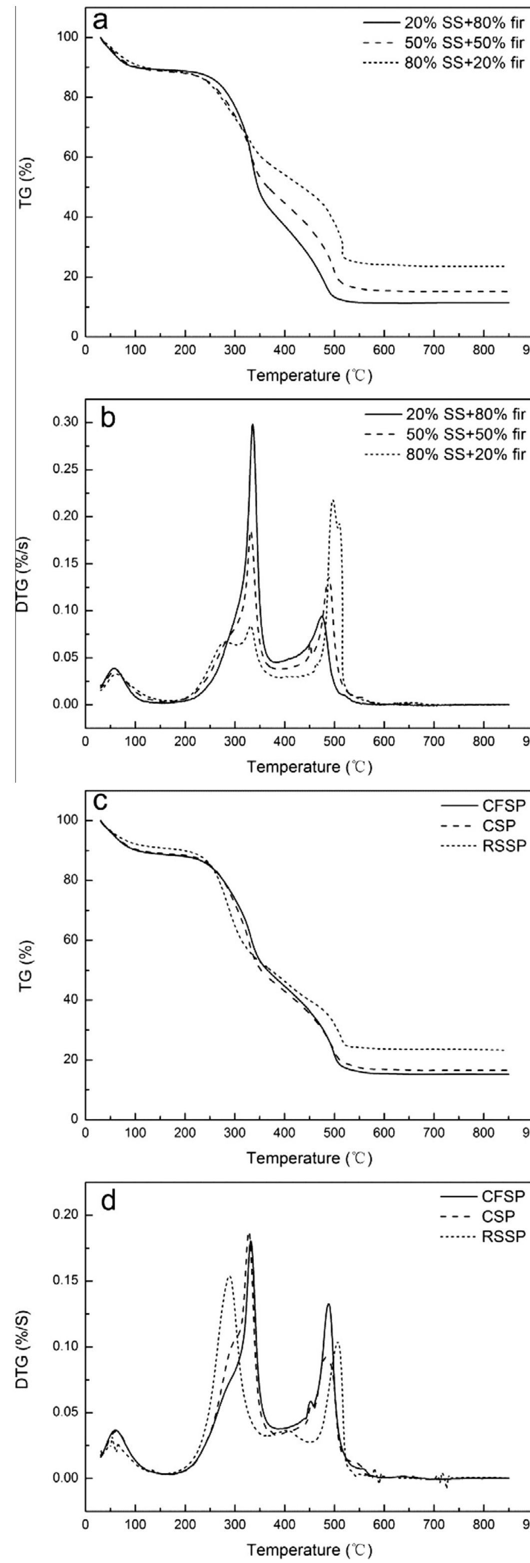

Fig. 6. TG and DTG curves of pellets with different amount of sludge (a, b) and different kind of biomass (c, d) in an air flow rate of 100 mL/min at a heating rate 15 °C/min.

The ignition temperature was estimated from the TG and DTG curves according to the method mentioned by Wang et al. (2009) and Zhao et al. (2013). The final combustion temperature was defined as the temperature that 99% of the combustible material has been burnt out (Zhao et al., 2013). As shown in Fig. 6a and c, each of the TG curves from all samples had four typical combustion

Table 2
The characteristic combustion parameters for pellets from blends of sludge and biomass.

Pellet sample	Ignition temperature (°C)	Final combustion temperature (°C)	Temperature at maximum weight loss rate (°C)	Maximum weight loss rate (%/s)	Residue (%)
20% SS + 80% fir	282	515	336	0.30	11.47
50% SS + 50% fir	265	554	332	0.19	15.16
80% SS + 20% fir	286	578	497	0.22	23.47
50% SS + 50% camphor	252	553	328	0.19	16.50
50% SS + 50% straw	221	559	289	0.15	23.29

stages, representing the dewatering phase, the combustion of volatile matter, the combustion of fixed carbon and burnout. From Fig. 6a and b, it was clearly seen that the pellet would have lower volatile weight loss rate and higher char burning rate with increasing sludge ratio. It was consistent with the increased density and hardness at higher sludge ratio case described in Section 3.2, which indicated that good bonding between particles would slow down the release of volatile. However, the higher sludge ratio pellet had increased residues after combustion (Fig. 6a and Table 2). As shown in Table 2, the sludge ratio in the pellet can be found to have little effect on the ignition temperature and final combustion temperature. Comparing the combustion of CFSP, CSP and RSSP, it was found that the characteristic combustion parameters of CFSP and CSP had little difference. The combustion of RSSP had lower ignition temperature and maximum weight loss rate, which indicated that the RSSP combusted in a more moderate way (Liu et al., 2014). However, the RSSP had higher residues after combustion.

The higher heating values of all pellets were determined using an oxygen bomb calorimeter from three replicates. It was found that the HHV of pellets was independent of process parameters (pressure, temperature and moisture content), but was highly affected by the heating value of raw material and the amount of sludge.

4. Conclusions

The natural binders coated on the particles are primarily lignin and protein. In addition, the synergistic effect of protein and lignin is the mechanism in the co-pelletization of sludge and biomass, and protein in the sludge is the main binder. As the low *Tg* of protein, the addition of sludge to wood pellet industry can reduce the stringent requirements of process parameters (especially pressure and temperature). Moreover, it can reduce the harm on hardness caused by the heterogeneity of biomass. Co-pelletization of sludge and biomass could be an alternative fuel technique according to the combustion characteristics and HHV of pellets.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.05.077.

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