The densification of cocoa bean shells for bioenergy purposes

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Highlights

- Cocoa bean shells were successfully densified into pellets
- Particle size reduction and higher compaction stresses improved pellet integrity
- The addition of bentonite clay enhanced pellet strength
- A direct relationship was found between pellet strength and resistance to abrasion and impact
- All investigated pellets exceeded the calorific value requirement of ISO 17725-6 for Grade A ‘non-woody’ pellets.
Abstract

The densification of cocoa bean shells into pellets was investigated to evaluate their potential as an alternative bioenergy source. The effect of shell particle size, compaction stress, compaction speed and binder addition was studied to ascertain the optimum processing conditions to produce the highest quality pellet. Compressive and tensile strength testing was employed to evaluate the mechanical integrity of the pellets, alongside their resistance to abrasion, impact and water. The results indicated that particle size reduction (to < 1 mm) and the addition of a binder were required to achieve acceptable pellet quality. Water, magnesium stearate and bentonite clay were selected as binding agents based on their industrial viability, accessibility and low cost. It was found that the addition of water or magnesium stearate was detrimental to pellet strength, whereas bentonite clay was found to enhance the strength. Pellets with added bentonite clay were subjected to combustion analysis to ascertain pellet moisture, ash content, elemental composition and calorific value. Promisingly, all pellets with added bentonite clay exceeded the 14.5 MJ kg⁻¹ calorific value requirement set by ISO 17225-6 standards for Grade A ‘non-woody’ pellets.

Key words:

- Biomass densification
- Compaction
- Cocoa bean shell
- Waste
- Pellet
- Combustion
Nomenclature

\[ d_{50} \] Particle size at 50% of cumulative mass fraction (m)

\[ d_{95} \] Particle size at 95% of cumulative mass fraction (m)

\[ D \] Pellet diameter (m)

\[ F_{\text{max}} \] Maximum force (N)

\[ h_v \] Latent heat of vaporisation of water (J kg\(^{-1}\))

\[ H \] Hydrogen content (mass fraction) of pellet (-)

\[ L \] Pellet length (m)

\[ M \] Moisture content (mass fraction) of pellet (-)

\[ \rho_0 \] Initial \textit{in situ} pellet density at applied compaction stress \( \sigma_0 \) (kg m\(^{-3}\))

\[ \sigma_0 \] Applied compaction stress within particle rearrangement regime (Pa)

\[ \sigma_{1,2} \] Transition stress to primary, secondary compaction regimes (Pa)

\[ \sigma_a \] Axial compressive strength (Pa)

\[ \sigma_t \] Radial crushing (tensile) strength (Pa)

\[ \text{CAPEX} \] Capital expenditure

\[ \text{CBS} \] Cocoa bean shell

\[ \text{CSP} \] Cocoa shell particulates

\[ \text{DTG} \] Derivative thermogravimetric

\[ \text{GCV} \] Gross calorific value

\[ \text{IRI} \] Impact resistance index

\[ \text{ISO} \] International Organisation for Standardisation

\[ \text{MgSt} \] Magnesium stearate

\[ \text{NCV} \] Net calorific value

\[ \text{OPEX} \] Operational expenditure

\[ \text{PDI} \] Pellet durability index

\[ \text{TGA} \] Thermogravimetric analysis
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1 Introduction

Global climate targets, formalised in the 2015 UN Paris Agreement, are aiming to keep the increase in average global temperature within 2°C above pre-industrial levels, whilst pursuing efforts to limit the increase to 1.5°C [1]. Commitments to such agreements require the diversification and securitisation of the global energy supply through the adoption of carbon-neutral, renewable technologies. According to the ‘2018 Key Energy Statistics’ from the International Energy Agency, 9.8% of the world’s total primary energy supply can be attributed to ‘biofuels and waste’ [2]. There is now a need to expand the current global portfolio of available biomass materials and increase their utilisation by sustainable means on an industrial scale.

The fruits of the cocoa tree (*Theobroma cacao*) are cocoa pods, each containing 20-50 cocoa beans surrounded by a white pulp [3]. Currently, four to five million tonnes of cocoa beans are harvested annually, predominantly from West Africa, namely Côte d’Ivoire (32%), Ghana (19%) and Nigeria (8%) [4]. The cocoa harvest has almost doubled over the past 30 years due to educating cocoa farmers with enhanced agricultural techniques through initiatives such as Cargill’s ‘Cocoa Promise’ [5]. Cocoa beans are processed to obtain cocoa nibs that are subsequently roasted and milled to produce cocoa liquor, the prime ingredient in chocolate manufacturing. Cocoa bean shell (CBS) (Figure 1), accounting for 10-12% of the bean mass, is removed via breaking, winnowing and aspiration processing [6]. Widely regarded as a waste product in the cocoa industry, the shell is predominantly disposed of in landfill or sold as a bulking agent in animal feedstock, despite its comparable gross calorific value (GCV) with commonly used biomass materials, as shown by Table 1. There is significant concern over harvesting biomass for energy purposes at the detriment of the food supply and indigenous land use. However, densifying CBS provides an opportunity to capitalise on the rebranding of a waste product from the cocoa industry as an alternative bioenergy source. The total addressable market for CBS utilisation is approximately 500,000 tonnes per annum [4]. The low ‘as-received’ bulk density of CBS renders transportation, even over short distances, economically unattractive. However, pelletisation increases the mass and energy density of biomass, alongside improving material handling and enabling use in standard combustion equipment [7]. Some main findings from research associated with cocoa-based and other materials used for bioenergy purposes are summarised in Table 2.
1.1 Pelletisation process parameters

Regarding definitions, much of the work in the literature uses the term ‘pellet’ to describe a cylinder of 3-27 mm diameter and 3-31 mm length, whereas the term ‘briquette’ describes a 18-55 mm diameter, 10-100 mm length cylinder [16]. However, ISO 17225-6 standards specify that the term ‘pellet’ may be used for cylinder diameters and lengths below 25 mm and 40 mm, respectively [17].

The authors of relevant literature commonly evaluate the effect of compaction pressure, compaction speed, particle size and holding time on biomass briquette quality. Bazargan et al. [18] focussed on fine tuning process parameters, such as compaction speed, to improve briquette production rates. Briquette strength was found to be highest when compacting finer particles, whereas the effect of compaction holding time was insignificant; it was also found that lower compaction speeds led to the formation of stronger briquettes. The addition of a binder (liquid and/or solid) generally increases the hardness, strength and durability of pellets through strengthening the bonds formed between particles [16]. Inorganic binders, such as bentonite clay, are inexpensive and abundant in resource but contribute to increased ash content, whereas organic binders enhance combustion performance but are expensive and have poor thermal stability [19]. However, the addition of water provides the most accessible and economical binder known to increase pellet mechanical strength. Bazargan et al. [7] refer to the three-fold effect of water addition to biomass samples, namely promoting solid bridge formation, increasing van der Waal’s forces and decreasing the glass transition temperature.

1.2 Quality testing and combustion of pellets

Following biomass densification in industry, pellets are subjected to compressive, shear and impact forces during storage and transportation to the end-user. Pellet quality testing indicates the effectiveness of the agglomeration process, assessing the strength and durability of the bonds formed during compaction [20]. However, as shown by Gilvari et al. [16], there is an absence of standardised testing and thus the development of dedicated standards for quality assessment of biomass pellets is required. Compressive strength testing simulates the forces acting during conveying, chuting and discharging into storage silos or freight trucks. According
to Richards [20], it was necessary for industrial fuel briquettes to maintain compressive strengths above 0.35 MPa, with a target of 0.375 MPa, and direct relationships between strength, abrasion resistance and impact resistance were observed. It was argued that tensile testing via radial crushing, i.e. employing the weaker orientation, yields the most practical measure of pellet strength, as densified biomaterials encounter multi-directional forces during transportation and therefore fail more frequently in the radial orientation [16]. Bazargan et al. [18] set a minimum strength requirement of 0.375 MPa for palm kernel shell briquettes. However, this value was incorrectly applied to the radial crushing (i.e. tensile) strength as opposed to the axial compressive strength. In a review of the literature, Gilvari et al. [16] highlighted the common deviation from the standard testing methodology for abrasion resistance, enlisted to simulate the vibrational forces experienced during conveying and haulage. Researchers were found to use a variety of sieve sizes in their studies of abrasion resistance, from 1.56 mm to 40 mm, although the standard sieve size should be 3.15 mm. Therefore, the durability values reported in the literature are unacceptable from the standard or practical point of view. Richards [20] introduced the impact resistance index (IRI), the most practical diagnostic of pellet strength, based on the number of drops and subsequent broken pieces generated from a stationary drop test. Biomass has been described as inherently hydrophilic and hygroscopic, naturally adsorbing and absorbing moisture from its environment, due to its natural fibrous structures and presence of hydroxyl groups in polysaccharides, even after densification [21]. It is therefore necessary to perform water resistance testing in order to simulate the outcome of pellet exposure to rain and humidity. Bazargan et al. [18] set a maximum criterion for briquette water resistance of 5 wt% water absorption upon immersion for 30 minutes.

The most important parameter for determining the effectiveness of a biomass fuel is calorific value, indicative of pellet energy potential [22]. For example, Christoforou and Fokaides [11] obtained direct calorific value measurements, alongside moisture, ash content and elemental analysis, of a number of agro-residue and wood pellets for comparison with ISO 17225-2/6 standards for ‘woody’ and ‘non-woody’ pellets. In comparison with ‘woody’ biomass materials, ‘non-woody’ pellets have a higher ash content and produce ashes with lower melting temperature [17], which aligns with the findings of Christoforou and Fokaides [11]. Knowledge of pellet ash content is found to be critical for residue management, particulate matter emissions and optimal design of combustion equipment. Most of the experimental studies in the literature employ thermogravimetric analysis of biomaterials to determine ash
Nitrogen and sulphur content are also deemed key parameters, since the reduction of the formation of nitrogen and sulphur oxides during combustion is an important environmental consideration, alongside preventing equipment corrosion [22].

1.3 Motivation for current study

The current experimental study involves the compaction of CBS into pellets to mitigate the issue of a low bulk density waste product from the cocoa industry. The aim is to produce the highest quality CBS pellet, in terms of the apparent density and mechanical robustness, via the investigation of feed material particle size, compaction parameters and addition of binders. Pellet quality is quantified through the testing of strength (axial compressive and radial crushing) and resistance (abrasion, impact and water). Pellet formulations that pass the quality testing criteria introduced in this study are subjected to combustion analysis, where properties of moisture, ash content and calorific value are evaluated to ascertain the validity of utilising CBS for bioenergy purposes. To the authors’ best knowledge, there has been no published research on the densification of CBS, and hence this study could be attractive for application within the cocoa and bioenergy sector.
2 Materials and Methods

All bench-top experiments were performed in a temperature- and humidity-controlled laboratory, with values recorded as 20-23°C and 33-39%, respectively. For the current study, the effects of temperature and humidity were not considered, although it is appreciated that these processing conditions could vary considerably during large-scale industrial pelleting processes.

2.1 Cocoa bean shell characterisation

2.1.1 Physical properties

As-received CBS (Cargill Cocoa and Chocolate, York, UK) had an irregular lamellae shape, deep brown colour and chocolatey odour. Solids density was estimated via an immersion test, where 20 g of CBS, in intervals of 2.0 g, was added to a 250 mL borosilicate glass measuring cylinder, containing 150 mL of toluene (anhydrous, 99.8%, Alfa Aesar 41464). The gradient of the mass versus volume displacement plot (Appendix Figure A1) provided an estimate of CBS solids density of 1880 ± 50 kg m⁻³.

2.1.2 Particle size distribution and bulk densities

To investigate the effect of particle size on pellet integrity, particle size reduction of CBS was performed using a Ninja Complete Food Processor with Auto-iQ using the processor vessel and accompanying chopper blades. The shaft speed was set to approximately 6000 rpm, corresponding to a blade tip speed of 42 ± 4 m s⁻¹. The 1.8 L processor vessel was filled with approximately 100 g of as-received CBS, which was then processed for 10 minutes to form cocoa shell particulates (CSP). The particle size distribution for all investigated particle sizes was determined using a nest of sieves, fixed on a Endecotts Model EVS 1 Sieve Shaker and set at an amplitude of 1 mm for 10 minutes. An example size distribution for as-received CBS is provided in Appendix Figure A.2a, where the data are fitted with a normal distribution curve. This procedure was also followed to obtain the processed, 1-2 mm and < 1 mm CSP size categories, as described in Table 3, where 50 and 95 (by mass) are reported; derived from Appendix A.2b. Bulk densities were determined by reading the volume, before and after tapping, of a known sample mass in a 500 mL borosilicate
glass measuring cylinder fixed to a Quantachrome Tapped Density Analyser set for 1000 taps, with reported errors being determined from three repeat tests. The Hausner ratio, indicative of the material flowability [23], was calculated as the ratio of tapped and as-poured densities.

2.1.3 Chemical composition

The chemical composition of the as-received CBS was obtained via combustion analysis performed by Socotec Ltd (Burton-on-Trent, UK); the subsequent absolute values for components of interest are provided in Table 4. Moisture content was determined in accordance to ISO 181343 [24], where pellets of known mass were heated in a stream of moisture-free nitrogen at 107°C for 4 hours in a Vindon oven; the moisture content was determined from the mass loss. The total content of carbon, hydrogen and nitrogen was determined using an Exeter Analytical CE440 Elemental Analyser, in accordance with ISO 16948 [25]. Sulphur content was determined using an Eltra CS580 analyser, in accordance with ISO 16994 [26]. Ash content was determined using a Carbolite Gero muffle furnace, in accordance with ISO 18122 [27], where pellets of known mass were held at 250°C for 60 minutes, then heated to 550°C over 50 minutes and held for 120 minutes; the residual mass was considered to be ash.

2.2 Binders

Three binders were chosen for the study (Table 5), viz. bentonite clay, magnesium stearate and deionised water. Studies have shown that bentonite clay, added in amounts of 6-8 wt%, promotes solid particle bonding and increases the fuel burn-out ratio during combustion [19]. Magnesium stearate is commonly employed in pharmaceutical compaction as a lubricant to reduce the wall frictional forces during ejection, and can be blended with granular materials in additions up to 5 wt% [28]. Deionised water was chosen due to its standard availability and low cost. Each binder was mixed with CSP for 5 minutes in a Kenwood Cooking Chef Stand Mixer (model KCC9060S) using the lowest speed setting.

2.3 Compaction

Uniaxial compaction of the material was performed using a Zwick Z050 mechanical strain frame (Figure 2a) containing an integrated load cell and displacement transducer, with resolutions of ± 0.1 N and ± 1 μm, respectively. A stainless-steel cylindrical ram with a high-
density polyethylene tip attached to a moving cross-head was used to compact the samples at ram velocities between 0.2 and 5.0 mm s\(^{-1}\) until the desired force (maximum of 30 kN) was attained. Cylindrical pellets were produced in a 11.2 mm diameter stainless-steel (316 SS) compaction cell (Figure 2b), where the barrel of the cell was screwed into a housing which acted as the bottom platen. The sample mass for pelletisation, containing CSP and any binder, was kept constant at 4.02 g; after filling into the compaction cell, the sample was initially tamped down using the tip of the ram to minimise the initial particle rearrangement phase that occurred during machine compaction. The Zwick software recorded the applied force and ram displacement over time. The applied stress was calculated by dividing the applied force by the cross-sectional area of the ram tip (11.0 mm in diameter); applied stresses ranged from 50 to 300 MPa. Pellets were ejected from the dismantled compaction cell using the moving ram. The typical height of the ejected pellets ranged from 28 to 35 mm (measured using Vernier callipers to ± 0.1 mm). Negligible change in diameter (11.2 mm) was observed for all ejected pellets. The mass of the pellets was determined using a Sartorius 1412 MP8-1 balance (± 0.01 g).

The elastic compliance of the compaction cell and Zwick Z050 assembly was accounted for using the displacement-force relationship presented in Appendix Figure A.3. Pellet densities were estimated from the measured values of pellet mass and volume (assuming a right cylinder). The reported \textit{in situ} densities refer to the ‘corrected density’ of the pellet inside the cell during compaction (\textit{i.e.} taking into account the elastic compliance of the apparatus), and the \textit{ex situ} densities refer to those of the ejected pellets. The \textit{ex situ} porosity of a given pellet was determined using Equation 1:

\[
\text{ex situ porosity of pellet} = 1 - \frac{\text{volume of solids in pellet}}{\text{ex situ volume of pellet}}
\]

The volume of the solids in the pellet was estimated using the mass and corresponding solids density of the CBS and of any binders (Table 5).

\textbf{2.4 Quality testing}

\textbf{2.4.1 Axial compressive and radial crushing strength}
For strength testing, each pellet was placed in a stable orientation onto a stationary stainless-steel base platen (Figure 3). A ram with a brass-block attachment (60 × 80 mm cross-section) was lowered onto the pellet using the Zwick strain frame at a speed of 0.2 mm s⁻¹. For the axial compressive strength (Figure 3a), a load was applied to the pellet (of diameter D) until failure occurred, where the maximum force, $F_{\text{max}}$, was recorded. The axial compressive strength, $\sigma_a$, was calculated using Equation 2 [20]:

$$
\sigma_a = \frac{4F_{\text{max}}}{\pi D^2}
$$

For a pellet of diameter $D$ and length $L$, orientated as shown in Figure 3b, the radial crushing strength, $\sigma_r$, also known as the tensile strength, was calculated using Equation 3 [7]:

$$
\sigma_r = \frac{2F_{\text{max}}}{\pi DL}
$$

Examples of the recorded force-displacement curves are provided in Appendix Figure A.4. Strength was represented as a force per unit area, as opposed to force, to remove the dependence of pellet size and shape [20]. Strength values were reported as the average of three separate strength tests carried out per pellet per orientation. A target of 0.375 MPa was applied to both compressive and tensile strengths, to maintain the same criterion for both orientations.

2.4.2 Abrasion resistance

ISO 17831-1 describes the standard durability procedure for abrasion resistance, where 500 g of pellets are placed in a tumbling box run at 50 rpm, whilst using a 3.15 mm sieve to quantify the remaining pellets in the apparatus, after 10 minutes of tumbling, as a percentage of the sample mass [29]. In this laboratory-based study, it was deemed impractical to produce 500 g of pellets for each investigated formulation over three repeat tests in order to comply with the standard durability test. Therefore, an overall praxis for abrasion resistance, quantified by the pellet durability index (PDI), was developed in-house, where a single pellet was placed in an Endecotts Model EVS 1 Sieve Shaker, using a 3.15 mm top sieve size, and set to an amplitude of 1 mm for 20 minutes. The remaining mass of the pellet was then used to quantify pellet durability as a percentage of the initial pellet mass. A PDI criterion of above 80% was set. The adoption of this non-standardised method supports the findings of Gilvari et al. [16], in that the
literature commonly deviates from the standard procedure for abrasion resistance, arguably due to the labour intensity of single pelletisation in the laboratory against the 500 g sample mass requirement of the ISO 17831-1 standard [29].

2.4.3 Impact resistance

Impact resistance was quantified by repeatedly dropping each pellet from a stationary height of 2 m onto a solid surface until pellet fracture occurred. The impact resistance index (IRI) was calculated using Equation 4 by recording the average of two tests for both the number of drops and the number of pieces the pellet broke into. An IRI value of 50 was set as the minimum acceptable value for pellets developed for industrial applications, as recommended by Richards [20].

\[
IRI = 100 \times \frac{\text{Average number of drops}}{\text{Average number of pieces}} \quad (4)
\]

2.4.4 Water resistance

Water resistance was determined via immersion testing, where a single pellet was placed in a room temperature (20-23°C) water bath of 25 mm depth (250 mL beaker, 70 mm diameter × 90 mm height) for 30 minutes. Intact materials were removed, wiped clean of surface water, left to dry for 30 minutes on a laboratory bench and then weighed. Water resistance was quantified by the mass of the intact pellet as a percentage of the initial mass; a criterion of above 50% water resistance was set.

2.5 Scanning electron microscopy (SEM)

An FEI Nova NanoSEM was employed, operating at 5–10 kV with a field-free lens, to analyse the fracture planes of pellets that failed via axial compressive testing (Section 2.4.1), in order to provide evidence of the fracture mechanism, and hence elucidate how the addition of a given binder contributes to pellet strength. The fracture plane surfaces were sputter-coated in a thin layer of palladium prior to examination. Pellets compacted with water as binder could not be analysed as a vacuum could not be achieved in the SEM chamber due to high moisture content.

2.6 Combustion analysis
A thermogravimetric analyser (Mettler Toledo TGA/DSC 1 STARe system) was used to assess the evolution of mass of the materials during combustion. A sample of known mass, containing < 212 μm CSP, was placed in an alumina crucible and heated from 50 to 900°C, then cooled back to 50°C. The total gas flow was 150 mL min⁻¹, with 100 mL min⁻¹ of purge and a protective stream of argon, alongside 50 mL min⁻¹ of air delivered above the crucible.

Analysis of pellet combustion properties was performed by Socotec Ltd (Burton-on-Trent, UK), as described in Section 2.1.3. GCV was also determined by Socotec Ltd using a Parr 6400 Automatic Isoperibol Calorimeter in accordance with ISO 18125 [30].
3 Results and Discussion

3.1 Compaction and pellet strength studies

Figure 4a displays a typical in situ compaction curve for CSP, exhibiting a reduction in densification rate at higher applied compaction stresses; it also indicates the importance of taking into account the elastic compliance of the apparatus (see Appendix Figure A.3) for calculating the corrected in situ density of a pellet.

Figure 4b reveals three distinct ‘regimes’ when the applied compaction stress is plotted on a logarithmic scale, namely the particle rearrangement, primary compaction and secondary compaction regimes; such regimes are a common finding in powder compaction studies [31]. Logarithmic trendlines can be fitted to the data within each regime in order to obtain parameters representing in situ densification rates, which can provide relative measures of powder compressibility [32]. Particle rearrangement is characterised by non-permanent elastic deformation of CSP at relatively low applied stresses, typically from 0 to 2.5 MPa, and is only active during the period of applied stress [7]. The transition at \( \sigma_1 \) to the primary compaction regime is taken as an indication of the start of permanent plastic deformation of the material due to interparticle bonding. The transition at \( \sigma_2 \) is taken as the start of the secondary compaction regime, where elastic deformation of the nearly non-porous bulk material occurs at relatively high applied stresses, typically around 100 MPa [18].

Relevant parameters obtained from the compaction data analysis of binderless CBS and CSP samples are displayed in Table 6 for different final applied compaction stresses and compaction speeds. The applied stress values at which the transitions to the primary and secondary compaction regimes occur, viz. \( \sigma_1 \) and \( \sigma_2 \), were identified by fitting logarithmic trendlines to the in situ data. The symbol \( \rho_0 \) is chosen to denote an initial in situ pellet density achieved at a given applied stress of \( \sigma_0 \), which is kept arbitrarily constant at 0.1 MPa.

3.1.1 Effect of particle size

Four categories of sample were investigated in terms of particle size, viz. as-received CBS, processed CBS, 1–2 mm CSP, and < 1 mm CSP. Forceful tamping down within the cell prior
to machine compaction was required for the as-received, processed and 1–2 mm samples, compared to the relative ease of sample preparation using < 1 mm CSP.

Compaction experiments were performed in triplicate. Photographs of pellets obtained for binderless samples compacted to a final applied stress of 300 MPa at a compaction speed of 0.2 mm s⁻¹ are shown in Figure 5. The < 1 mm CSP pellet (Figure 5d) has a visibly smoother and non-cracked surface compared to the others; this can be explained by the larger surface area to volume ratio of < 1 mm CSP, leading to an increased number of particle-wall and interparticle contact points during compaction [7]. Pellets obtained from the < 1 mm CSP samples were the only ones to retain 100% of the initial sample mass (see Table 6). The values of σ₁ indicate that higher applied stresses (and hence compaction time) are required for samples containing larger particles to transition from the initial particle rearrangement to primary compaction regimes; however, all samples transition to the secondary compaction regime at a similar applied stress of σ₂ = 100 MPa.

Referring to the data in Table 6, for a given final applied compaction stress of 300 MPa and compaction speed of 0.2 mm s⁻¹, the in situ final pellet density is greatest for the as-received CBS sample. However, the axial elastic relaxation of the pellets upon ejection appears to be more prevalent for those containing larger particles: pellets formed using as-received, processed, 1-2 mm and < 1 mm samples exhibit approximately 33%, 24%, 24% and 21% decreases in density upon ejection, respectively, due to an associated increase in pellet height for the mass retained. (It should be noted that large amounts of elastic relaxation during the ejection of compacted pellets, caused by higher amounts of elastic energy stored in the pellet, can induce defects such as cracks, capping and lamination [33].) Thus the ex situ pellet density is the least for the as-received CBS sample, with all other pellets displaying similar values of 1200 – 1220 kg m⁻³, corresponding to pellet porosities of approximately 0.36 – 0.35, respectively.

From an industrial perspective, although the compaction of < 1 mm CSP samples produces pellets of greater integrity, pulverising as-received CBS into a fine powder is a highly energy-intensive process, necessitating additional pre-processing steps. However, for the current laboratory-based study, the < 1 mm CSP material was chosen for subsequent pellet formation for reasons based on the ease of sample preparation and improved integrity of pellets.
3.1.2 Effect of final applied compaction stress

The effect of the final applied compaction stress for < 1 mm CSP samples on ex situ pellet density and strength was investigated. The data in Table 6 show that 100% of the compacted mass is retained during pellet ejection for all conditions studied. For a given compaction speed of 0.2 mm s\(^{-1}\), as the final applied compaction stress increases from 50 to 300 MPa, the ex situ pellet density increases (porosities reducing from 0.40 to 0.35, respectively). The formation of solid bridges, integral for pellet strength, is more likely to be achieved at higher applied stresses by facilitating the diffusion of molecules inbetween particles and reducing sample porosity, thereby producing a higher pellet density [18]. Densities obtained from three repeat tests are displayed in Figure 6, and appear to follow a linear trend with the logarithm of final applied compaction stress. Such a trend is in common with those reported for ceramic powder compaction studies [31] and more recently for palm kernel shell biochar compaction [7].

The difference between the values of final in situ and ex situ densities implies a higher degree of axial elastic relaxation for pellets compacted to higher final applied stresses (viz. density decreases of approximately 13% for 50 MPa vs 21% for 300 MPa), due to initiation of the secondary compaction regime (the start of elastic compaction of the bulk material).

Pellet strengths were found to increase with increasing final applied compaction stress, as shown by Figure 7. The results confirm that radial crushing strength is considerably less than axial compressive strength, with the pellets formed at 100 MPa and above exceeding the specified minimum strength target of 0.375 MPa. Industrial pellet mills and roll presses typically operate at compaction stresses of 100-150 MPa [34], so it is promising to observe acceptable pellet strengths here.

Although the highest strengths occur for pellets compacted to 300 MPa, higher applied stresses in industry induce a constraint on pellet production rate, due to an extended machine run time, and necessitate heavier-duty equipment, thereby increasing CAPEX requirements [18]. Additionally, higher OPEX requirements for high-stress compaction are a consequence of increased energy demand and maintenance frequency due to accelerated equipment wear. However, for the current study, a final applied compaction stress of 300 MPa was chosen for subsequent pellet formation, based on the characteristics of highest strength and ex situ density.
3.1.3 Effect of compaction speed

The data in Table 6 for < 1 mm CSP samples compacted to a final applied stress of 300 MPa suggest that both the final in situ and ex situ pellet densities are independent of the compaction speed for the range studied. Typically, the test times to reach an applied stress of 300 MPa during compaction were approximately 10, 40 and 200 s for compaction speeds of 5.0, 1.0 and 0.2 mm s$^{-1}$, respectively. The value of $\sigma_1$ increases with increasing compaction speed, indicative of a reduced opportunity for particle rearrangement at higher speeds. There is no evident relationship between the pellet elastic relaxation and the compaction speed; all pellet final densities decrease upon ejection by 20-22%.

The pellet strength data in Figure 8 suggest that axial compressive strength decreases with increasing compaction speed, which aligns with the findings of Bazargan et al. [18] for the compaction of palm kernel shell; this result may indicate that less effective interparticulate bonding occurs during shorter compaction times. The radial crushing strengths of the pellets appear to be independent of the compaction speed within the reproducibility range of the tests. The relatively large range bars observed for the 5 mm s$^{-1}$ tests could be explained by an applied stress overshoot of up to 25 MPa during sample compaction. A recommendation for future study would be to reduce the transient response time of any compaction equipment to ensure compaction ceases promptly once the target stress is achieved.

For these single pelleting tests, it is promising to see that the compaction speed has a minimal effect on pellet strength. From an industrial perspective, the ability to attain a higher production rate without compromising pellet durability would be advantageous; however, this inter-relationship would need to be verified for any given large-scale processing equipment employed.

3.1.4 Effect of binder

Varying amounts of each of the three binders listed in Table 5 were mixed with < 1 mm CSP and pellets formed with 4.02 g of the material compacted to a final applied stress of 300 MPa
at a speed of 0.2 mm s\(^{-1}\). Experiments were performed in triplicate. Relevant parameters obtained from the subsequent study are displayed in Table 7.

3.1.4.1 Water as binder

Room-temperature water was added to CSP as a softening agent, since it cannot be compacted as a free liquid. The data in Table 7 shows a reduction of pellet mass retention with increasing water content due to partial pellet degradation and possible water loss. A trend of decreasing \(\sigma_2\) values and increasing in situ final pellet densities is seen with increasing water content, although ex situ densities remain similar at all water additions studied. The pellet elastic relaxation appears to be similar for all water contents, with pellet densities decreasing upon ejection by 22-23%. Formulations with water additions above 8.0 wt% led to excess water movement into the free space of the equipment, which proved challenging for pellet ejection and separating the compaction cell from its housing. A decrease in pellet strength with increasing water content is displayed in Figure 9. Pellets formed with 6.0 and 8.0 wt% water did not achieve the minimum radial crushing strength criterion of 0.375 MPa. Overall, the results suggest that water does not act as a cementing binder [7].

3.1.4.2 Magnesium stearate as binder

Following the recommendation of Morin and Briens [28], magnesium stearate (MgSt) was employed as an inexpensive, chemically stable lubricant. Table 7 shows that only two formulations were considered in the current study, and hence any trend in the parameters with MgSt addition cannot be identified. However, comparing the results with those obtained for the binderless pellet, the addition of MgSt reduces the final in situ and ex situ densities, although the ex situ pellet porosities are similar. There is also a comparative reduction in elastic relaxation upon ejection (14-16% decrease in density). Figure 10 suggests that the addition of MgSt is detrimental to pellet strength, with the 5.0 wt% pellet failing to achieve the minimum radial crushing strength criterion of 0.375 MPa.

Figure 11 displays a micrograph of the fracture plane for the 5.0 wt% MgSt pellet after axial compressive failure, and provides evidence of the occurrence of intergranular fracture; the apparent smooth surface and interparticle fissures signify poor particle adhesion, suggesting adhesive failure between the surfaces of adjacent particles [35].
3.1.4.3 Bentonite clay as binder

Bentonite clay was selected as a binder based on its bonding capability and global economic availability, and was added to CSP in intervals up to 8.0 wt%, following the recommendations of Zhang et al. [19]. Table 7 indicates an increase in both final in situ and ex situ pellet densities with increasing bentonite clay addition; the estimated porosities of the ejected pellets decrease from 0.34 to 0.33 accordingly. There appears to be a slight increasing trend of pellet elastic relaxation with increasing binder addition, with pellet densities decreasing upon ejection from 20 to 22%. As with the addition of water, increasing the amount of bentonite clay causes a decrease in $\sigma_2$. Figure 12 shows that pellet strength increases with increasing bentonite clay addition, with all pellets studied achieving the minimum radial crushing strength criterion of 0.375 MPa.

A micrograph of the fracture plane for the 8.0 wt% bentonite clay pellet after axial compressive failure is shown in Figure 13a. In contrast to the smooth-looking fracture plane for the MgSt-bound pellet (Figure 11), the rough uneven surface suggests a high-energy transgranular fracture. Upon further magnification (Figure 13b&c), the presence of fibrous structures implies that adhering CSP fragments have been torn apart due to cohesive failure of solid lignin bridges [35]. The results suggest that the addition of bentonite clay enhances interparticle adhesion, thus producing pellets with higher mechanical integrity.

3.1.4.4 Summary of the binder effects

Figure 14 summarises the radial crushing (tensile) strength data as a function of ex situ pellet density for all samples investigated. For the solid binders (MgSt and bentonite clay), there appears to be a positive correlation between the two parameters. Interestingly, this trend is not followed for the water-bound pellets, which exhibit a decreasing strength with increasing pellet density. Although a strength-density relationship for CSP compaction with solid binders is observed, a universal correlation cannot be stated since density alone does not incorporate the effectiveness of interparticle bonding for different formulations [20]. However, it could be argued that the higher specific gravity of bentonite (see Table 5) was responsible for the higher ex situ density and pellet strength, due to the addition of more dense particles.
### 3.2 Quality testing

In addition to axial compressive and radial crushing strength studies, the pellet formulations listed in Table 7 were subjected to quality testing to quantify the pellet resistances to abrasion (PDI), impact (IRI) and water, with minimum targets of 80%, 50 and 50%, respectively. In order to progress to a combustion analysis, a given pellet formulation was expected to exceed all criteria set by the minimum standards.

The data in Table 8 confirm that direct relationships exist between pellet radial crushing strength and both PDI and IRI values, namely that stronger pellets have higher resistances to both abrasion and impact, aligning with the findings of Richards [20]. Pellets produced with higher water and MgSt contents fail to meet the radial crushing strength criteria. Bentonite clay-bound pellets are the only formulations to exceed the 80% minimum threshold for PDI. Richards [20] defined a PDI minimum of 95% for multiple briquettes in a tumbling drum. However, as only a single pellet was used in the current study, the effect of abrasive forces experienced between a group of pellets was not determined, rendering PDI comparisons with the literature unreliable [16]. The IRI criterion of 50 is achieved by all the pellets studied, demonstrating exceptional impact resistance, particularly for the bentonite clay-bound pellets.

All the pellets were found to fail the water resistance methodology outlined by Richards [20], as partial pellet degradation occurred upon immersion. Therefore, the procedure was modified to quantify water resistance as the mass of the intact pellet as a percentage of initial pellet mass, as outlined in Section 2.4.4. The data in Table 8 suggest that the addition of the chosen binders increases the pellet water resistance. In summary, the results indicate that only the bentonite clay-bound pellets exceed all the quality-testing criteria. Therefore, these pellets were taken forward for combustion analysis.

### 3.3 Combustion analysis

Figure 15 displays the results from the thermogravimetric analysis (TGA) along with the corresponding differential thermogravimetric (DTG) plot for the combustion of a sample of CSP (<212 μm particle size) up to 900°C. The TGA curve shows that combustion of CSP follows three distinct stages that are identified by a rapid increase in the DTG values, namely
the release of free water (drying), decomposition of organic matter (devolatisation) and combustion of char. The first stage, from 50-120°C, is responsible for approximately 7.0% of mass loss and can be attributed to the elimination of water, with a maximum DTG peak at 60°C. The largest mass loss of 56.3% occurs in the second stage, predominantly as a result of the degradation of cellulose, hemicellulose and pectin [10], with a maximum DTG peak at 300°C. The final combustion stage begins at approximately 420°C, with a maximum DTG peak at 440°C, where the decomposition of the residual carbon skeleton occurs [36]. The residual mass of 12.4% can be attributed to ash content. The discrepancy between this value obtained from TGA and the 9.3% value reported in Table 4 is most likely due to the difference in analysis equipment and final temperature of the tests compared to those employed by Socotec Ltd (viz. Section 2.6 and Section 2.1.3, respectively). Further contributions to this discrepancy may also be due to undecomposed organic material and inorganic compounds remaining in the sample, alongside any inherent measurement error when using a CSP sample mass of < 0.01 g.

For the CSP/bentonite clay material, the TGA in Figure 16 confirms that the addition of the binder increases ash content upon combustion, as the residual mass of the CSP sample with 8.0 wt% bentonite clay is approximately 2.2% higher than that for the binderless CSP sample.

Table 9 presents the combustion analysis results for the 2.0, 4.0 and 8.0 wt% bentonite clay / CSP pellets, in comparison with ISO 17725-6 standards for graded ‘non-woody’ pellets [17]. This standard encompasses herbaceous, fruit and aquatic biomass pellets; for use in residential and commercial buildings, alongside industrial energy generation applications which require classified pellet quality [17]. The net calorific value (NCV) of each pellet was calculated using Equation 5 [37], where $H$ and $M$ are the hydrogen and moisture contents (mass fractions) of a given pellet, respectively, and $h_v$ is the latent heat of vaporisation of water (2.26 MJ kg$^{-1}$):

$$\text{NCV} = \text{GCV} - (9H + M)h_v \quad (5)$$

The data suggest a direct relationship between pellet carbon content and calorific value, as expected. All investigated pellets exceeded the minimum requirements for the calorific value of Grade A ‘non-woody’ pellets set by ISO 17225-6 [17], thereby demonstrating exceptional bioenergy potential. The moisture content of all investigated pellets is lower than the 10 wt% threshold set by the ISO 17225-6 Grade A standard [17]. The results suggest that sulphur content increases with increasing bentonite clay addition, with the 8.0 wt% bentonite
clay / CSP formulation exceeding the maximum limit of 0.2 wt% for the ISO 17225-6 Grade A standard [17]. The high inherent fuel-bound nitrogen content in CBS (see Table 4) and bentonite clay-bound CSP pellets exhibits non-compliance with ISO 17225-6 standards [17] and gives rise to the generation of NO\(_x\) emissions upon combustion, thereby confirming that industrial utilisation should be accompanied by comprehensive abatement measures, such as selective non-catalytic reduction [38]. Although the 2 wt% bentonite clay / CSP formulation complies with the ISO 17725-6 Grade B standard [17] for ash content, the 9.9 wt% value obtained may be subject to reproducibility error due to the close margin against the standard. In addition, the high ash content may result in operational issues upon combustion, such as fouling, slagging and corrosion inside boilers and flue gas systems [17]. Therefore, due to the high nitrogen and ash content in the investigated pellets, it is recommended to use specifically designed pellet burners or boilers for CSP applications.
4 Conclusions

It has been demonstrated that cocoa bean shell (CBS), an industrial waste product, can be compacted in the laboratory to form cylindrical pellets of aspect ratio ~3. The compaction of < 1 mm cocoa shell particulates (CSP) was found to exhibit the most favourable properties of a densified biomaterial, namely the highest *ex situ* pellet density, a visibly smoother surface and minimal elastic relaxation upon ejection. A positive correlation between the final applied compaction stress and both the axial compressive and radial crushing (tensile) strengths of the pellets was observed, alongside an inverse relationship between compaction speed and axial compressive strength of the pellets.

Bentonite clay was the only investigated binder found to enhance the mechanical strength of the CSP pellets. Quality testing verified a direct relationship between pellet strength and resistances to abrasion (PDI) and impact (IRI). The observed pellet degradation during water resistance testing confirmed that CSP pellets should not be subjected to wet conditions for prolonged periods, therefore storage with waterproof coverings is recommended. The calorific data for the bentonite clay-bound pellets demonstrated the high bioenergy potential of CBS. However, thermogravimetric and elemental analysis revealed a relatively high ash and nitrogen content, respectively, which could pose operational and environmental challenges during combustion in pellet burners or boilers on an industrial scale.

This study has provided a first step towards validating the use of CBS as a biomass fuel, providing evidence of compliance to multiple parameters of the ISO 17225-6 standard. Further study would need to consider the economic impact of adopting the selected processing conditions in industry, as there is a trade-off between increasing the mechanical strength of the pellets with the cost of the feed preparation, compaction process and equipment maintenance requirements. The effect of the variation of process parameters, such as temperature and humidity, on the compaction behaviour and subsequent pellet quality would also be an important factor. The consideration of the bulk density of a larger volume of pellets, imperative to packaging, transport and marketing of pellets, would also be advantageous.
References


Anuar, M., Briscoe, B. The elastic relaxation of starch tablets during ejection, *Powder Technology*, **195** (2) (2009), 96-104.


Table 1: Gross calorific values (GCV) of various biomass material [8].

<table>
<thead>
<tr>
<th>Biomass material</th>
<th>GCV (MJ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood chips</td>
<td>18.5 – 21.0</td>
</tr>
<tr>
<td>Cocoa bean shell (CBS)</td>
<td>18.5 – 20.1</td>
</tr>
<tr>
<td>Hazelnut shell</td>
<td>19.0 – 19.3</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>18.3 – 19.2</td>
</tr>
<tr>
<td>Palm kernel shell</td>
<td>17.7 – 19.0</td>
</tr>
</tbody>
</table>
Table 2: Summary of main findings from literature on relevant materials used for bioenergy purposes (listed chronologically).

<table>
<thead>
<tr>
<th>Material</th>
<th>Main findings</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cocoa pod husk (CPH)</td>
<td>• GCV of 17.0 MJ kg(^{-1})</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>• Burning time increased with increased carbonisation of CPH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Carbon monoxide emission factor increased with increased portion of carbonised husk in pellet</td>
<td></td>
</tr>
<tr>
<td>Cocoa bean shell (CBS)</td>
<td>• Use of a polycaprolactone matrix for testing under tensile loading and morphological characterisation</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td>• Thermogravimetric analysis suggested degradation of hemicellulose, pectin and cellulose at 313°C</td>
<td></td>
</tr>
<tr>
<td>Olive husk</td>
<td>• Pelletised agro-residues used for bioenergy purposes</td>
<td>[11]</td>
</tr>
<tr>
<td>Walnut shells</td>
<td>• Ash content of untreated wood shavings and exhausted olive husk found to be higher than acceptable level of 10 wt%</td>
<td></td>
</tr>
<tr>
<td>Wood shavings</td>
<td>• All pellets exceeded ISO standards for calorific values of biomass pellets (&gt; 14.5 MJ kg(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>Bagasse</td>
<td>• Addition of binders found to increase particle adhesion, pellet strength, abrasion resistance and energy content</td>
<td>[12]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>• Binders reduced cost of producing pellets by reducing required compaction stress, conditioning temperature and maintenance frequency</td>
<td></td>
</tr>
<tr>
<td>Binder: Biosolids</td>
<td>• Characterisation of CBS bio-compounds for applications in food industry</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>• Source of fibre, high in phenolics, antioxidant agent</td>
<td></td>
</tr>
<tr>
<td>Cocoa bean shell (CBS)</td>
<td>• Binder promoted solid bridge formation between particles during compaction</td>
<td>[14]</td>
</tr>
<tr>
<td>Coffee husk</td>
<td>• Binder caused weakening of solid-solid interactions</td>
<td></td>
</tr>
<tr>
<td>Rice husk</td>
<td>• Densification increased energy density by up to 600% for rice husk</td>
<td></td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>• High water resistance of pellets with added binder</td>
<td></td>
</tr>
<tr>
<td>Binder: Crude glycerol</td>
<td>• Pelletisation of food waste after hydrothermal carbonisation</td>
<td></td>
</tr>
<tr>
<td>Municipal solid waste</td>
<td>• Solid-bridge formation due to binder recrystallisation increased pellet compressive strength, density and impact resistance</td>
<td>[15]</td>
</tr>
<tr>
<td>Binder: Cane molasses</td>
<td>• Use of binder increased water resistance and lowered ignition temperature</td>
<td></td>
</tr>
</tbody>
</table>
Table 3: CBS and CSP particle size and bulk density data, with errors determined from three repeat tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_{50}$ (mm)</th>
<th>$d_{95}$ (mm)</th>
<th>As-poured density (kg m$^{-3}$)</th>
<th>Tapped density (kg m$^{-3}$)</th>
<th>Hausner ratio</th>
<th>Flow character [23]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received CBS</td>
<td>7.87</td>
<td>12.2</td>
<td>140 ± 10</td>
<td>155 ± 10</td>
<td>1.10</td>
<td>Excellent</td>
</tr>
<tr>
<td>Processed CBS</td>
<td>1.90</td>
<td>3.23</td>
<td>405 ± 40</td>
<td>495 ± 40</td>
<td>1.22</td>
<td>Fair</td>
</tr>
<tr>
<td>1–2 mm CSP</td>
<td>1.47</td>
<td>1.95</td>
<td>410 ± 10</td>
<td>465 ± 10</td>
<td>1.13</td>
<td>Good</td>
</tr>
<tr>
<td>&lt; 1 mm CSP</td>
<td>0.47</td>
<td>0.95</td>
<td>560 ± 50</td>
<td>635 ± 50</td>
<td>1.14</td>
<td>Good</td>
</tr>
</tbody>
</table>
Table 4: Moisture, CHNS and ash content of as-received CBS obtained via combustion analysis (performed by Socotec Ltd, Burton-on-Trent, UK).

<table>
<thead>
<tr>
<th>Component</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>10.2</td>
</tr>
<tr>
<td>Carbon</td>
<td>46.3</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.6</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.7</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.2</td>
</tr>
<tr>
<td>Ash</td>
<td>9.3</td>
</tr>
</tbody>
</table>
Table 5: Solid powder and liquid binders (specific gravity of solids from suppliers).

<table>
<thead>
<tr>
<th>Binder</th>
<th>Supplier</th>
<th>$d_{95}$ (mm)</th>
<th>Specific gravity</th>
<th>Addition (wt%)</th>
<th>Addition (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite clay (sodium form)</td>
<td>Alfa Aesar</td>
<td>0.15</td>
<td>2.50</td>
<td>2.0 – 8.0</td>
<td>1.5 – 6.1</td>
</tr>
<tr>
<td>Magnesium stearate</td>
<td>LFA Tablet Presses</td>
<td>0.15</td>
<td>1.03</td>
<td>2.5 – 5.0</td>
<td>4.5 – 8.8</td>
</tr>
<tr>
<td>Deionised water</td>
<td>-</td>
<td>N/A</td>
<td>1.00</td>
<td>2.0 – 8.0</td>
<td>3.1 – 14.0</td>
</tr>
</tbody>
</table>
Table 6: Effect of processing parameters on pellet mass retention, compaction curve parameters ($\sigma_0$ taken as 0.1 MPa) and densities. The values reported are the average of compaction tests performed in triplicate. All samples had an initial mass of 4.02 g and no binder present. A dash indicates that the compaction regime was not attained.

<table>
<thead>
<tr>
<th>Set parameters</th>
<th>Variable parameter</th>
<th>Mass retained (%)</th>
<th>$\sigma_1$ (MPa)</th>
<th>$\sigma_2$ (MPa)</th>
<th>$\rho_0$ (kg m$^{-3}$)</th>
<th>$\text{In situ}$ final density (kg m$^{-3}$)</th>
<th>$\text{Ex situ}$ density (kg m$^{-3}$)</th>
<th>Ex situ porosity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final applied compaction stress 300 MPa</td>
<td>CBS/CSP sample</td>
<td>As-received</td>
<td>86.6</td>
<td>10</td>
<td>100</td>
<td>540</td>
<td>1750</td>
<td>1170</td>
</tr>
<tr>
<td>Compaction speed 0.2 mm s$^{-1}$</td>
<td></td>
<td>Processed</td>
<td>96.0</td>
<td>7.5</td>
<td>100</td>
<td>560</td>
<td>1600</td>
<td>1210</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1–2 mm</td>
<td>99.0</td>
<td>5.0</td>
<td>100</td>
<td>565</td>
<td>1580</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 1 mm</td>
<td>100</td>
<td>2.5</td>
<td>100</td>
<td>610</td>
<td>1540</td>
<td>1220</td>
</tr>
<tr>
<td>Sample &lt; 1 mm CSP</td>
<td>Final applied compaction stress (MPa)</td>
<td>50</td>
<td>100</td>
<td>2.5</td>
<td>—</td>
<td>610</td>
<td>1285</td>
<td>1120</td>
</tr>
<tr>
<td>Compaction speed 0.2 mm s$^{-1}$</td>
<td></td>
<td>100</td>
<td>100</td>
<td>2.5</td>
<td>—</td>
<td>610</td>
<td>1445</td>
<td>1160</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>100</td>
<td>2.5</td>
<td>100</td>
<td>610</td>
<td>1490</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>100</td>
<td>2.5</td>
<td>100</td>
<td>610</td>
<td>1540</td>
<td>1220</td>
</tr>
<tr>
<td>Sample &lt; 1 mm CSP</td>
<td>Compaction speed (mm s$^{-1}$)</td>
<td>0.2</td>
<td>100</td>
<td>2.5</td>
<td>100</td>
<td>610</td>
<td>1540</td>
<td>1220</td>
</tr>
<tr>
<td>Final applied compaction stress 300 MPa</td>
<td></td>
<td>1.0</td>
<td>100</td>
<td>3.5</td>
<td>100</td>
<td>610</td>
<td>1550</td>
<td>1230</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>100</td>
<td>5.0</td>
<td>100</td>
<td>610</td>
<td>1550</td>
<td>1240</td>
</tr>
</tbody>
</table>

*Ex situ porosity estimated using value of 1880 kg m$^{-3}$ for solids density of CBS/CSP.
Table 7: Effect of binder addition on pellet mass retention, densities and compaction curve parameters, for 4.02 g of < 1 mm CSP and binder, compacted to a final applied stress of 300 MPa at 0.2 mm s\(^{-1}\) (\(\sigma_0 = 0.1\) MPa, \(\rho_0 = 610\) kg m\(^{-3}\)). The values reported are the average of compaction tests performed in triplicate.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Binder addition (wt%)</th>
<th>Mass retained (%)</th>
<th>In situ final density (kg m(^{-3}))</th>
<th>Ex situ density (kg m(^{-3}))</th>
<th>(\sigma_1) (MPa)</th>
<th>(\sigma_2) (MPa)</th>
<th>Ex situ porosity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>100</td>
<td>1540</td>
<td>1220</td>
<td>2.5</td>
<td>100</td>
<td>0.35</td>
</tr>
<tr>
<td>Water</td>
<td>2.0</td>
<td>98.5</td>
<td>1565</td>
<td>1225</td>
<td>3.0</td>
<td>90</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>97.0</td>
<td>1585</td>
<td>1225</td>
<td>3.0</td>
<td>80</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>96.0</td>
<td>1590</td>
<td>1230</td>
<td>3.0</td>
<td>70</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>94.5</td>
<td>1595</td>
<td>1230</td>
<td>3.0</td>
<td>60</td>
<td>–</td>
</tr>
<tr>
<td>Magnesium stearate</td>
<td>2.5</td>
<td>100</td>
<td>1430</td>
<td>1200</td>
<td>2.5</td>
<td>90</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>100</td>
<td>1390</td>
<td>1190</td>
<td>2.5</td>
<td>80</td>
<td>0.34</td>
</tr>
<tr>
<td>Bentonite clay</td>
<td>2.0</td>
<td>100</td>
<td>1560</td>
<td>1250</td>
<td>2.5</td>
<td>95</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>100</td>
<td>1585</td>
<td>1260</td>
<td>2.5</td>
<td>90</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>100</td>
<td>1610</td>
<td>1270</td>
<td>2.5</td>
<td>85</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>100</td>
<td>1640</td>
<td>1280</td>
<td>2.5</td>
<td>80</td>
<td>0.33</td>
</tr>
</tbody>
</table>

*Ex situ* porosity estimated using Equation 1. Porosities of water-bound pellets unable to be estimated due to loss of sample mass of unknown composition.
Table 8: Radial crushing strength, PDI, IRI and water resistance values for the pellet formulations listed in Table 7 (4.02 g pellets of < 1 mm CSP and binder, compacted to a final applied stress of 300 MPa at 0.2 mm s\(^{-1}\)). The shaded boxes indicate a failure to meet the specified minimum target.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Binder addition (wt%)</th>
<th>Radial crushing strength (MPa)</th>
<th>PDI (abrasion) (%)</th>
<th>IRI (impact)</th>
<th>Water resistance (%)</th>
<th>Pass/Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum target</td>
<td>–</td>
<td>0.375</td>
<td>80</td>
<td>50</td>
<td>50</td>
<td>F</td>
</tr>
<tr>
<td>None</td>
<td>0.0</td>
<td>0.47</td>
<td>77.4</td>
<td>75</td>
<td>38.0</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
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<td>P</td>
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<td>0.53</td>
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Table 9: Combustion properties of 2.0, 4.0 and 8.0 wt% bentonite clay / CSP pellets, compared to ISO 177225-6 standards [17]. A dash signifies no available ISO 177225-6 standard.

<table>
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<th></th>
<th>ISO 17725-6 A [17]</th>
<th>ISO 17725-6 B [17]</th>
<th>2.0 wt% bentonite/CSP</th>
<th>4.0 wt% bentonite/CSP</th>
<th>8.0 wt% bentonite/CSP</th>
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<td>–</td>
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<td>–</td>
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<td>14.5</td>
<td>16.1</td>
<td>15.5</td>
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*Values calculated using Equation 5
Figure 1: Cocoa bean shell (CBS) (as supplied by Cargill Cocoa and Chocolate).
Figure 2: (a) Experimental compaction set-up using Zwick Z050 strain frame and (b) plan view of 11.2 mm diameter compaction cell containing tamped CSP sample.
Figure 3: Experimental set-up and orientation of pellets for (a) axial compressive and (b) radial crushing strength testing (adapted from [18]).
Figure 4: *In situ* compaction curves for $< 1$ mm CSP (4.02 g sample) on (a) linear and (b) logarithmic applied compaction stress scales. The corrected density (red line) is determined by incorporating the effects of the elastic compliance of the compaction apparatus. Labels 0, 1 and 2 in (b) represent the particle rearrangement, primary and secondary compaction regimes, respectively. Grey dashed vertical lines indicate transition to primary and secondary compaction regimes, occurring at stresses $\sigma_1$ and $\sigma_2$, respectively.
Figure 5: Pellets of diameter 11.2 mm formed using (a) as-received CBS, (b) processed CBS, (c) 1–2 mm CSP, and (d) < 1 mm CSP. All samples had initial mass of 4.02 g and no binder present, and were compacted to a final applied stress of 300 MPa at speed 0.2 mm s⁻¹.
Figure 6: Effect of final applied compaction stress on *ex situ* pellet density for 4.02 g of < 1 mm CSP compacted at a speed of 0.2 mm s⁻¹. Note logarithmic scale for final applied compaction stress. The data point size indicates the range of density values over three tests. The dashed line represents the best-fit logarithmic trendline, as given by the equation shown.

\[ \text{Density} = 53.7 \ln(\text{Stress}) + 909 \]

\[ R^2 = 0.995 \]
Figure 7: Effect of final applied compaction stress on the average pellet axial compressive and radial crushing strengths, for 4.02 g of < 1 mm CSP compacted at a speed of 0.2 mm s\(^{-1}\), with strength range bars over three tests. Note the two strength scales differ by a factor of ten. The red dashed horizontal line indicates the minimum radial crushing strength criterion of 0.375 MPa.
Figure 8: Effect of compaction speed on the average pellet axial compressive and radial crushing strengths, for 4.02 g of < 1 mm CSP compacted to a final applied stress of 300 MPa, with strength range bars over three tests. Note the two strength scales differ by a factor of ten. The red dashed horizontal line indicates the minimum radial crushing strength criterion of 0.375 MPa.
Figure 9: Effect of water addition on the average pellet axial compressive and radial crushing strengths, for 4.02 g of < 1 mm CSP and binder compacted to a final applied stress of 300 MPa at a speed of 0.2 mm s$^{-1}$, with strength range bars over three tests. Note the two strength scales differ by a factor of ten. The red dashed horizontal line indicates the minimum radial crushing strength criterion of 0.375 MPa.
Figure 10: Effect of magnesium stearate addition on the average pellet axial compressive and radial crushing strengths, for 4.02 g of <1 mm CSP and binder compacted to a final applied stress of 300 MPa at a speed of 0.2 mm s\(^{-1}\), with strength range bars over three tests. Note the two strength scales differ by a factor of ten. The red dashed horizontal line indicates the minimum radial crushing strength criterion of 0.375 MPa.
Figure 11: SEM image (39 × magnification) of the fracture plane of the 5.0 wt% MgSt pellet (after axial compressive failure. Pellet formed from 4.02 g of <1 mm CSP and binder compacted to a final applied stress of 300 MPa at a speed of 0.2 mm s⁻¹.
Figure 12: Effect of bentonite clay addition on the average pellet axial compressive and radial crushing strengths, for 4.02 g of < 1 mm CSP and binder compacted to a final applied stress of 300 MPa at a speed of 0.2 mm s$^{-1}$, with strength range bars over three tests. Note the two strength scales differ by a factor of ten. The red dashed horizontal line indicates the minimum radial crushing strength criterion of 0.375 MPa.
Figure 13: SEM images of an 8.0 wt% bentonite clay pellet fracture plane (after axial compressive failure) at magnifications of (a) 39 ×, (b) 950 × and (c) 3500 ×. Pellet formed from 4.02 g of < 1 mm CSP and binder compacted to a final applied stress of 300 MPa at a speed of 0.2 mm s⁻¹.
Figure 14: Effect of *ex situ* pellet density on radial crushing strength. All pellets formed from 4.02 g of < 1 mm CSP and binder compacted to a final applied stress of 300 MPa at a speed of 0.2 mm s⁻¹. The blue, grey and red lassos cluster the data points for pellets compacted with water, MgSt and bentonite clay, respectively. The dashed line is employed to guide the reader’s eye.
Figure 15: TGA curve (red) and DTG plot (grey) for CSP. The black diagonal lines indicate the start of a new combustion stage in which mass losses for drying, devolatisation and char combustion phases are 7.0%, 56.3% and 24.3%, respectively, resulting in an overall mass loss of 87.6%. 
Figure 16: TGA curves for samples with CSP only (red) and CSP / 8.0 wt% bentonite clay (black).
Figure A.1: CSP mass addition plotted against volume displacement to determine solids density; the error bar shown indicates an example of the volume error of $\pm 0.5 \times 10^{-6} \text{ m}^3$ for the 250 mL borosilicate glass measuring cylinder. The dotted line represents the best-fit linear trendline through the origin, as given by the equation shown.

Mass = $1880 \times$ Volume

$R^2 = 0.999$
Figure A.2: Data points represent an average of triplicate tests and error bars show the data range. (a) Example particle size distribution by mass for as-received CBS. The black line represents a normal distribution curve fit to the midpoint sieve size data. (b) Cumulative distribution plot of each investigated sample on a logarithmic scale. The solid lines represent normal cumulative distribution curve fits to the upper sieve size data to determine $d_{50}$ and $d_{95}$ values.
Figure A.3: Elastic compliance of the compaction apparatus. The data points were obtained by applying a known ram movement within the empty compaction cell and recording the associated force. The dotted line represents the best-fit linear trendline, as given by the equation shown.

Displacement = 0.029 × Force + 0.146

$R^2 = 0.998$
Figure A.4: Examples of force-displacement curves obtained for axial compressive (black line) and radial crushing (red line) strength testing performed at a ram speed of 0.2 mm s$^{-1}$ for a pellet of 4.02 g of < 1 mm CSP (no binder) compacted to 300 MPa at a speed of 0.2 mm s$^{-1}$. Initial pellet dimensions of $D = 11.2$ mm and $L = 33.4$ mm. Grey dashed vertical lines indicate pellet failure. Inset photograph displays a fractured pellet after axial compressive testing.