International Journal of Recycling of Organic Waste in Agriculture (2020) 9: 119-135
DOI: 10.30486/IJROWA.2020.1889862.1018

ORIGINAL RESEARCH

Agricultural wastes as renewable fillers in physical granulation of NPK fertilizers: Evaluation of on-size granules and comparison to conventional filler

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Received: 21 May 2019 / Accepted: 23 March 2020 / Published online: 28 June 2020

Abstract

Purpose This research aimed to evaluate the yield and quality of granular NPK fertilizers prepared by physical granulation with eggshell, snail shell, and cow bone as fillers and to compare them to conventional filler.

Methods Urea, DAP, KCl, and fillers were milled separately and mixed to the desired formula. About 150 g of mixed powders were granulated on a disc granulator in 9 minutes, at a rotation speed of 35 rpm and a disc slope of 45°. Water at a desired additional moisture was sprayed on the tumbled powders to facilitate the granulation. The obtained granules were then dried and screened into three fractions: undersize (< 2 mm), on-size (2 to 4 mm), and oversize (> 4 mm).

Results Snail shells and eggshells as fillers were found to give on-size NPK granules having yield and compressive strength which were comparable to that with limestone as a conventional filler. For NPK 15-15-15, using snail shells and eggshells as fillers, the yields of on-size granules achieved 46% and 56%, respectively, and the compressive strengths of on-size granules reached 2.4 and 2.1 MPa, respectively. Cow bones as fillers resulted in low compressive strength. The distribution of nutrients in the NPK granules was found to be close to the targeted formula.

Conclusion Snail shells and eggshells as fillers have good yield and quality of on-size NPK granules and are very potential alternatives to limestone.

Keywords Disc granulator, Physical granulation, NPK fertilizer, Agricultural waste, Renewable filler

Introduction

NPK fertilizers are multinutrient fertilizers that contain all primary macroelements needed by the plants, i.e., nitrogen (N), phosphor (P), and potassium (K). NPK fertilizers can be prepared by blending or granulation. Blending in which granular fertilizers are physically mixed is a simple method, having low capital and operating costs. However, it is susceptible to segregation during storage and transportation. Because of that, bulk NPK fertilizers are mainly produced by granulation. There are two types of NPK granulation: reactive granulation and physical granulation. In the former, a slurry is first prepared through a chemical reaction, e.g., phosphoric acid is made to react with ammonia vapor to produce ammonium phosphate slurry. The slurry is then sprayed upon a tumbling bed of potassium chloride, recycled solid, filler and other solid materials to form NPK granules. Reactive granulation gives granules with excellent homogeneity. However, it is capital intensive due to the corrosivity of acid materials. Physical granulation, also called *fuse blending*, tumbles and granulates solid fertilizer mixtures with the addition of water (Doshi 1991). It requires less capital than reactive granulation but still gives excellent homogeneity.

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Fillers help to adjust the percentage of the nutrients to a desired ratio, prevent caking of the fertilizers, and increase the fertilizer weight (Gowariker and Krishnamurthy 2009). Fillers dilute the concentration of fertilizer active ingredients, which can burn roots and stems. Fillers are commonly taken from rock materials. One of the conventional filler materials is limestone. Limestone became popular since it is easily available and is a source of calcium, a secondary macronutrient, for plant nutrition. However, as a rock material, it is non-renewable, its reserve is, of course, limited. Alternatives for conventional fillers are necessary to create a more sustainable process production.

In seeking alternatives for materials, attention needs to be paid on agricultural wastes, among them are eggshells, snail shells, and cow bones. Many chemical products have been derived from wasted eggshells, snail shells, and cow bones, e.g., catalysts (Hu et al. 2011; Roschat et al. 2016; Laskar et al. 2018), adsorbents (Hossain et al. 2015; Abdulrahman et al. 2016), biomaterials (Abdulrahman et al. 2014; Brzezińska-Miecznik et al. 2015), organic fertilizers (Hamideh and Akbar 2018), and preservatives (Thakur et al. 2019). The applications of these wastes as fillers in making granular NPK fertilizers will give a new alternative for increasing the value-added of the agricultural sector and for reducing waste. As such wastes are renewable materials, their utilization as fillers will create a more sustainable NPK fertilizer process production. It will also provide additional benefits since such wastes can function as fertilizers or soil conditioners (King`ori 2011; Oliveira et al. 2013; Kouakou et al. 2015; Nogalska 2016; Paul et al. 2017).

According to HIS Markit Report (Business Wire 2020), the global demand for compound fertilizers is expected to be more than 151 million tons in 2023. Assuming a filler content range of 20% to 25%, for NPKs 15-15-15 and 20-10-10 made from a mixture of urea, diammonium phosphate (DAP), and potassium chloride (KCl), this demand means an annual need for at least 30 to 38 million tons of filler materials. According to FAO (2020), the global production of eggs, beef and snail meat in 2017 reached 80 million, 67 million, and 18 thousand tons, respectively. Eggshells represent 10% of the total weight of the eggs (King`ori 2011), bone represents 19% of the total weight of the cattle carcass (Afolayan et al. 2002), and the weight ratio of shell to meat in fresh snails is 30:41 (Iwanegbe et al. 2016). Thus, the residues from these three commodities alone are available at more than 20 million tons per year or about 53% to 67% of filler demand. The availability will certainly increase along with world population growth. Considering such a significant amount, the uses of these residues as alternative sources of fertilizer fillers are necessary to reduce environmental issues.

Granulation is a size enlargement process which uses a liquid binder to form interparticle bonds and agitates the powder-liquid mass to promote liquid dispersion and granule growth (Litster and Ennis 2004). Numerous works have been done on the granulation of fertilizers. Early works reported the effects of moisture, temperature, and formula in the granulation of fertilizer mixtures involving ammoniation (Hardesty and Ross 1938; Hardesty et al. 1956; Giddings and Delapp 1962; Giddings and DeLapp 1963; Boylan and Kamat 1964; Boylan and Johnson 1966). More intensive works on the effects of granulation parameters, including liquid-to-solid ratio, granulation time, fertilizer solubility, binder properties, and initial size distribution, have been done both on degree of granulation (Adetayo et al. 1993; Walker et al. 2000; Rodrigues et al. 2017) and strength of granules (Walker et al. 2003). The effects of the internal structure of solid binders (Xue et al. 2014) and the method of binder delivery on the granulation (Gluba 2003) have also been studied. Much progress has been achieved in understanding the granulation mechanisms (Iveson et al. 1996, 2001; Iveson and Litster 1998; Kapur and Runkana 2003; Reynolds et al. 2005; Roy et al. 2009). Studies on the modeling and control of granulation circuits have also been reported (Adetayo et al. 1995a,b; Cotabarren et al. 2009, 2010, 2011, 2013; Herce et al. 2017). Most publications are on the rotary drum but reports on other types of granulators are also available, such as disc granulators (Delwel and Veer 1978; Chadwick and Bridgwater 1997; Chai et al. 2017) and high shear granulators (Mangwandi et al. 2013a, b, 2014, 2015). The preparation of NPK fertilizers by physical granulation of fertilizer mixtures and agricultural wastes as fillers has not been studied intensively.

One problem that needs to be answered is whether substituting agricultural wastes for conventional fillers will affect the performance of NPK fertilizer granulation. Some important issues that need to be considered are yield and quality of on-size granule and how they are affected by granulation variables. The important quality parameters include granule strength and nutrition content. It is the purpose of this research to evaluate the yield and quality of NPK fertilizers prepared by physical granulation of mixed fertilizers and agricultural wastes as fillers and to compare the results with a conventional filler, limestone in this case. Limestone was chosen as a comparison because it has long been used as a fertilizer filler (Tidmore and Simmons 1934; Bauer et al. 2019), especially for acidic soils. The agricultural wastes studied were eggshell, snail shell, and cow bone. Besides as fillers, the presence of these agricultural wastes in the NPK granules is also expected to provide renewable calcium for plant nutrition. Urea, DAP, and KCl were used as the sources of primary macronutrients. Two N-P-K formulas, 15-15-15 and 20-10-10, which are commonly applied for horticultural and paddy in Indonesia, were studied. The granulation was carried out on a disc granulator as disc granulation is easy to operate, has low cost, and is commonly applied in fertilizer industries. Additional moisture content, one of the influential variables in physical granulation, was varied during the experiment to study its effects.

Materials and Method

Urea (46% nitrogen) and KCl (60% potassium as K_2O) fertilizers were purchased from a local distributor. DAP containing 15% nitrogen and 46% phosphor as P_2O_5 was kindly supplied by PT Petrokimia Gresik (a fertilizer company located in Gresik, East Java, Indonesia). Chicken eggshells were collected from a local cake shop. Shells of land snail *(Achatina fulica)* were obtained from a feed shop. Waste cow bones were obtained from a local restaurant. The meat flakes attached to the bones were removed manually. All solid materials were dried and milled until passing a screen of 80 mesh. None of the milled materials could pass a screen of 200 mesh so that the powders granulated had sizes in the range of 80 to 200 mesh.

Fig. 1 shows the schematic of the granulation apparatus used. The apparatus consisted of an inclined disc equipped with a scrapper, supported on a frame which allows slope adjustment. The disc was rotated by a motor equipped with a speed reducer and an inverter. The disc was made from acrylic, having a diameter of 40 cm and a rim height of 4 cm. The disc internal surface was covered with a floor sticker to avoid slippage between particles and disc surfaces. Water was sprayed through a sparger having a hole diameter of 0.2 mm connected to a mini compressor. Through a regulator, the compressor could supply compressed air at a constant pressure of 2 bar.

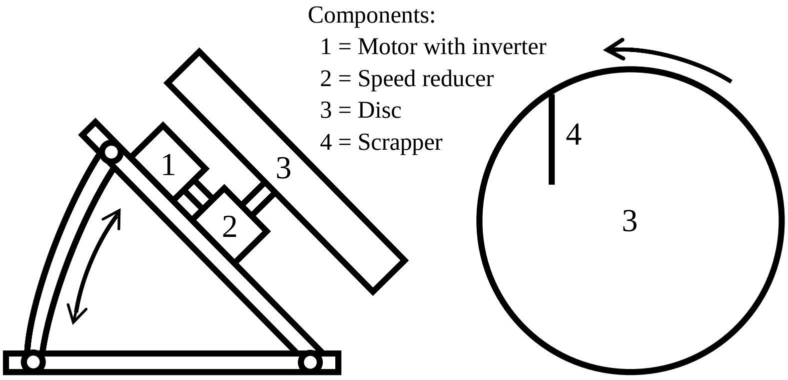


Fig. 1 Schematic of granulation apparatus

The granulation was carried out in a batch system. Before granulated, 150 g powdered materials were mixed in a blender for 15 seconds. The mixed powders consisted of urea, DAP, KCl, and filler. Filler was used to bring the nutrient percentages of the mixtures to the desired value. Two third of the mixed powder was then tumbled on the disc. After 15 seconds of rotation, water was then sprayed on the tumbled powders. After the soluble fertilizers dissolved in the sprayed water, coalescence occurred between particles. After a determined time, before the tumbled particles tend to collide to become one mass and stick to the disc surface, the rest one-third of the mixed powder was then poured into the disc. The growth of granules was then dominated by layering. This layering stage was made the same for all runs, i.e., 3 minutes. The granules were oven-dried at 80°C for two hours and continued at 50°C in 20 hours. The dried granules were then screened into three fractions: undersize (-10 mesh or ≤ 2 mm), on-size

(+10/-5 mesh or between 2 to 4 mm), and oversize (+5 mesh or ≥ 4 mm). Each fraction was packed in a polypropylene plastic with a silica gel pocket inside. Moisture content (additional) of 6% and granulation time of 9 minutes (including 3 minutes layering stage using one-third of powder mass) were used as a standard condition. The rotation speed and slope of the disc were kept constant at 35 rpm and 45°, respectively.

Compressive strength was measured on 10 to 20 on-size granules using a hardness tester (Tianjin Guoming Medicinal Equipment). The test equipment measured the maximum load that could be sustained by a granule. The load was converted to compressive strength in units of pressure by dividing the load by the projected area of the granule which was calculated from its diameter. The results were expressed as average strengths. Nitrogen content was measured using Kjeldahl method. Phosphor content as P_2O_5 was measured by spectrophotometry. Potassium content as K_2O was measured by atomic absorption spectroscopy. Calcium content was determined by titration with disodium ethylene diamine tetra-acetate (EDTA) according to the literature (Jeffery et al. 1989) after treating the sample with a hydrochloric acid solution. The crystalline structure of limestone, eggshell, snail shell, and cow bone powders were characterized by XRD (Bruker's D8 advance diffractometer) with Cu Kα radiation (1.54 Å) at 40 kV and 35 mA. The diffraction pattern was collected at a step size of 0.02° and a step time of 0.4 s in 2θ ranging from 5° to 100°. Infrared spectra were measured by a Bruker's Alpha FTIR spectrometer. Total organic matter (TOM) was determined as weight loss on ignition heating for 4 hours in a furnace at 560°C, following the literature (López et al. 2010). Water drop penetration time, defined as the time needed by a water drop to penetrate a mixed fertilizer filler powder and used here to describe hydrophobicity, was determined according to the literature (Doerr 1998).

Results and Discussion

Filler material characterization

Fig. 2 shows the XRD patterns of the fillers. The obtained patterns were interpreted by referring to the patterns of calcite, aragonite, and hydroxyapatite from the literature (Kontoyannis and Vagenas 2000; Ni and Ratner 2008; Gheisari et al. 2015; Xue et al. 2015). In the XRD patterns of limestone and eggshells, strong calcite peaks of $CaCO_3$ were observed. Most peaks in the XRD patterns of the snail shells and cow bones showed the existence of aragonite ($CaCO_3$) and hydroxyapatite, respectively. Consistent results were obtained from IR spectra as shown in Fig. 3. In comparison with the spectra of $CaCO_3$ (Jovanovski et al. 2002), it is evident that $CaCO_3$ was present as calcite in limestone (observed at 713, 874, and 1405 cm^{-1}) and in eggshells (observed at 713, 876, and 1418 cm^{-1}). On the other hand, the presence of $CaCO_3$ as aragonite in the snail shells was observed at 713, 858, and 1471 cm^{-1}. The presence of hydroxyapatite in the bones was confirmed by the bands at 3284 cm^{-1} due to -OH stretching vibration, at 1018 cm^{-1} due to asymmetric P-O stretching vibration, and at 600 and 560 cm^{-1} due to symmetric P-O stretching vibration. The double split peaks at 1413 and 1447 cm^{-1} were attributed by $CO_3^{=}$ which is also present in the bones. Other bands were at the regions of 2853-2919 cm^{-1} and 1642-1742 cm^{-1} corresponding to C-H and C=O stretching vibrations, indicating the presence of organic matter. The obtained XRD patterns and IR spectra are in align with early findings on limestone (Hwidi et al. 2018), eggshells (Engin et al. 2006; Naemchanthara et al. 2008), snail shells (Hu et al. 2011; Laskar et al. 2018), and bones (Akindoyo et al. 2017; Gao et al. 2017).

Table 1 shows the primary macronutrient contents, total organic matter (TOM), and moisture contents of the fillers used. Only cow bone showed significant content in macronutrient, namely phosphor. Cow bone also had another uniqueness; it contained the most organic matter, compared to the others. It also contained a significant amount of fatty materials. By using Soxhlet extraction, the bone was found to contain 17%-w fat. Its moisture was also higher than the others. By taking the non-organic matter as mineral part, the mineral content (%-w) of limestone, eggshells, snail shells, and cow bones were estimated to be 99.2, 94.6, 97.5, and 61.8, respectively. The main mineral in limestone, eggshells, and snail shells are the same, i.e., $CaCO_3$. By using a titration method, it was found that the contents of $CaCO_3$ in limestone, eggshells, and snail shells were 94, 94, and 97 %-w, respectively. The calcium content of the cow bone was found to be 23%-w. These values agree with the previous works found in the literature. The results from previous studies (Field et al. 1974; Keene et al. 2004; Khalil et al. 2017) showed that the calcium content of cow bone is in the 17-29 %-w range. Commercial limestone generally consists of over 90% $CaCO_3$ (Stanmore and Gilot 2005). Zaheer (2015) found chicken eggshells contain 94% calcium carbonate crystals. Molluscan shells, including snail shells, contain 95-99.9% $CaCO_3$ (Marxen et al. 2003). The significant difference between $CaCO_3$ and mineral contents in limestone indicated that limestone contains mineral components other than $CaCO_3$.

To obtain fertilizer mixtures with required N-P-K formulas, urea, DAP, KCl, and filler were blended in an appropriate composition. The compositions of formulas 15-15-15 and 20-10-10 are presented in Tables 2 and 3, respectively. Due to the existence of phosphor in cow bone, the N-P-K formulas with cow bone as fillers contain more filler, less DAP, and more urea compared to those with other materials as fillers.

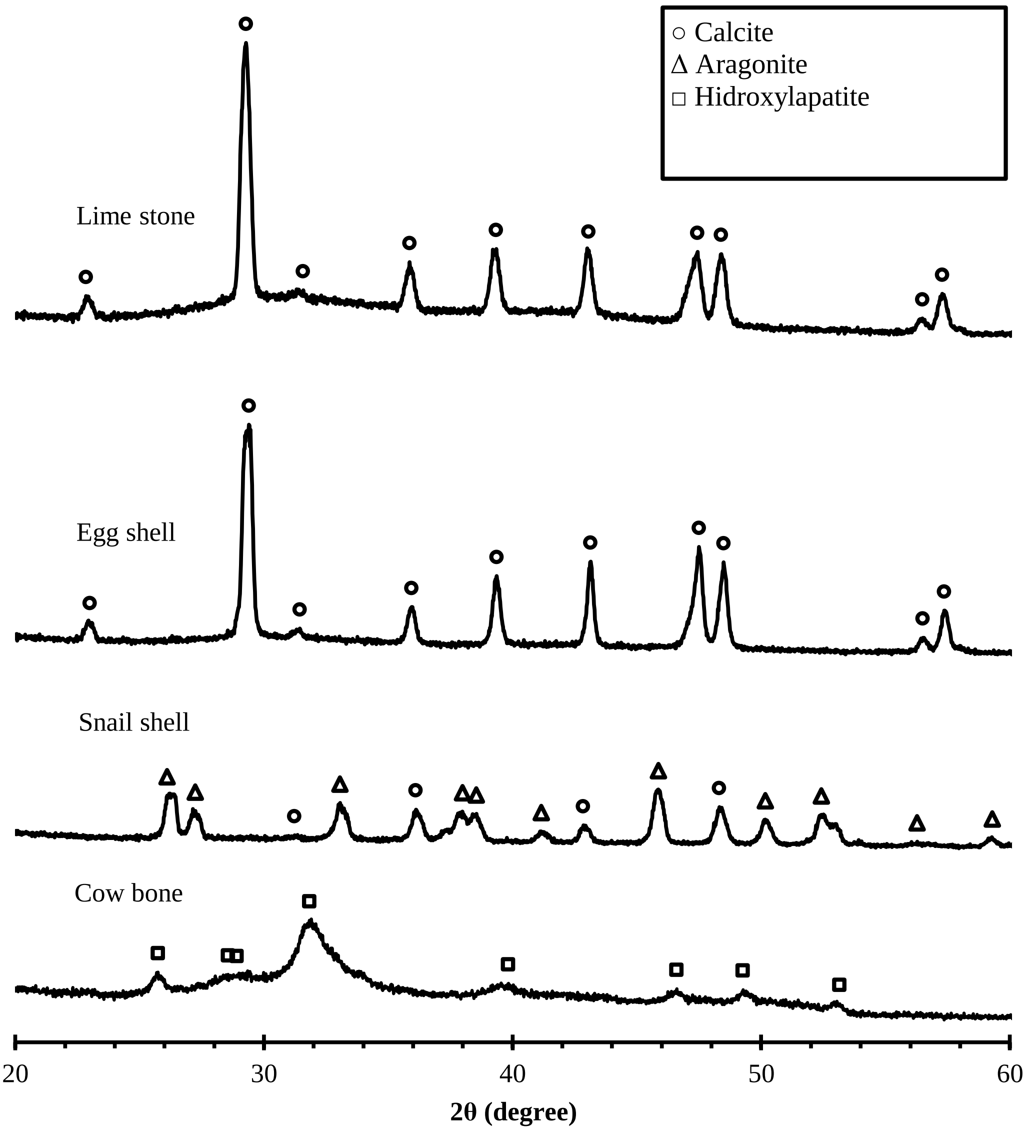


Fig. 2 XRD patterns of filler materials

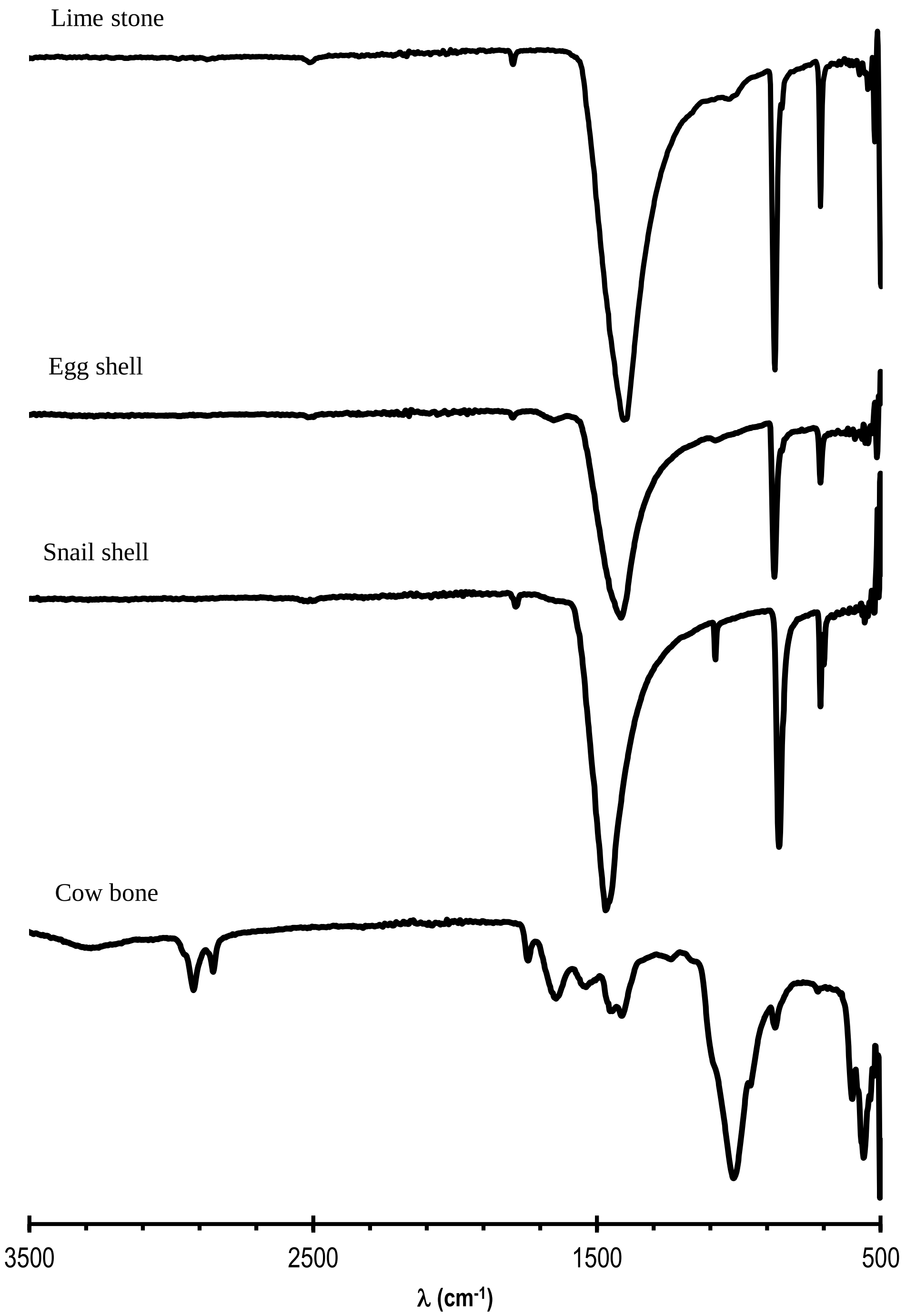


Fig. 3 IR spectra of filler materials

Table 1 Macronutrient analysis of fillers

Filler	N (%)	P (%-P_2O_5)	K (%-K_2O)	TOM (%)	Mineral (%)	Moisture (%)
Lime stone	≈ 0	≈ 0	≈ 0	0.8	99.2	0.04
Egg shell	0.85	0.31	0.04	5.4	94.6	0.67
Snail shell	2.88	0.05	0.04	2.5	97.5	0.18
Cow bone	0.12	18.91	0.12	38.2	61.8	2.81

Table 2 Composition of NPK 15-15-15

Filler material	Weight (%)			
	Urea	DAP	KCl	Filler
Egg shell	21.6	32.5	24.7	21.2
Snail shell	20.6	32.6	24.7	22.1
Cow bone	25.8	20.8	24.7	28.7
Lime stone	22.0	32.6	24.7	20.7

Table 3 Composition of NPK 20-10-10

Filler material	Weight (%)			
	Urea	DAP	KCl	Filler
Egg shell	36.0	21.5	16.5	26.0
Snail shell	34.7	21.7	16.5	27.1
Cow bone	41.0	7.2	16.4	35.4
Lime stone	36.4	21.6	16.5	25.5

Yield and Strength of On-size Granules

The yields of on-size NPK 15-15-15 granules with various fillers and at various additional moisture are illustrated in Fig. 4. All of the organic wastes used showed the same tendency in on-size yield as limestone. The yield of on-size granules increased with moisture content, reached a maximum at 6% moisture, and then fallen again on further increase in moisture content. The very low yield of on-size granule at low moisture content was due to the high undersize fraction, indicating a low degree of granulation. On the other hand, the very low yield at higher moisture content was caused by the high fraction of oversize, indicating an over granulation. Fig. 5 plots average diameter, which can be used to represent the degree of granulation, against additional moisture where diameters of 1, 3, and 5 mm were used to represent the sizes of undersize, on-size, and oversize fractions, respectively. The tendency of the influence of additional moisture on the degree of granulation for eggshell, snail shell, and cow bone as fillers were the same as limestone, the degree of granulation increased with additional moisture. Below 5% moisture, the curves are rather shallow, but above 5%-moisture, the curves become steep indicating high degrees of granulation. The rapid increase in average diameter above 5% additional moisture indicated an induction granulation mechanism. At additional moisture larger than 7%, the degree of granulation decreased indicating the occurrence of breakage phenomenon. The same trends were also observed by previous authors, in the granulation of sodium triphosphate (Delwel and Veer 1978), of ammonium sulfate, monoammonium phosphate, and diammonium phosphate (Adetayo et al. 1993), and of NPK made up of ammonium nitrate, ammonium phosphate, and potassium chloride (Walker et al. 2000). The results obtained here confirmed that the substitution of eggshell, snail shell, and cow bone for limestone as fillers in the NPK fertilizer granulation do not change the granulation behavior.

To obtain a standard error necessary to justify the significance of yield difference among the variations, a run using snail shell at 6% additional moisture was repeated four times. The confidence interval at 95% confidence level for the on-size fraction was found to be (46.5±4.0) %-w. With an error bar of ±4%, it can be said that the on-size yields were not significantly affected by the filler materials at most additional moistures except at 6%. At 6% additional moisture, both eggshell and snail shell gave on-size yields comparable to limestone. Cow bone as a filler, however, resulted in an on-size yield significantly lower than limestone. Based on the maximum yield of on-size granules, fillers followed the order: limestone ≈ eggshell ≈ snail shell > cow bone. It was found also that cow bone gave the highest undersize fraction. These results indicated that NPK 15-15-15 with cow bone as filler is most difficult to granulate than with the other two agricultural wastes.

The compressive strengths of on-size NPK 15-15-15 granules are illustrated in Fig. 6. The error bars and bullets represent confidence intervals at a 95% significance level and average values, respectively. For each filler material, the compressive strength of granules increased with moisture content. However, the slopes of the compressive strength curves decreased as moisture content increased. This resulted in the existence of a maximum compressive strength, as clearly seen for eggshells, cow bones, and limestone. Walker et al. (2003) found a proportional relationship between granule strength and liquid saturation. On the other hand, Rodrigues et al. (2017) found that granule strength decreases with increasing liquid-phase to solid ratio. The strength of granules is developed by the formation of crystal bridges between particles after drying. The strength of the crystal bridges is affected by many factors, such as moisture content or liquid-to-solid ratio, initial particle size distribution, organic content, shape irregularity, granulation time and temperature. Iveson et al. (2001) explained that the presence of maximum strength in fine particle systems is caused by the opposite effects of liquid content on inter-particle friction and liquid bridge capillary forces. Liquid content increases capillary forces which increase granule strength but, on the other hand, reduces interparticle frictions which lower strength. When capillary forces are dominant, granule strength increases with moisture content. In contrast, when the frictional forces dominate, adding moisture decreases granule strength.

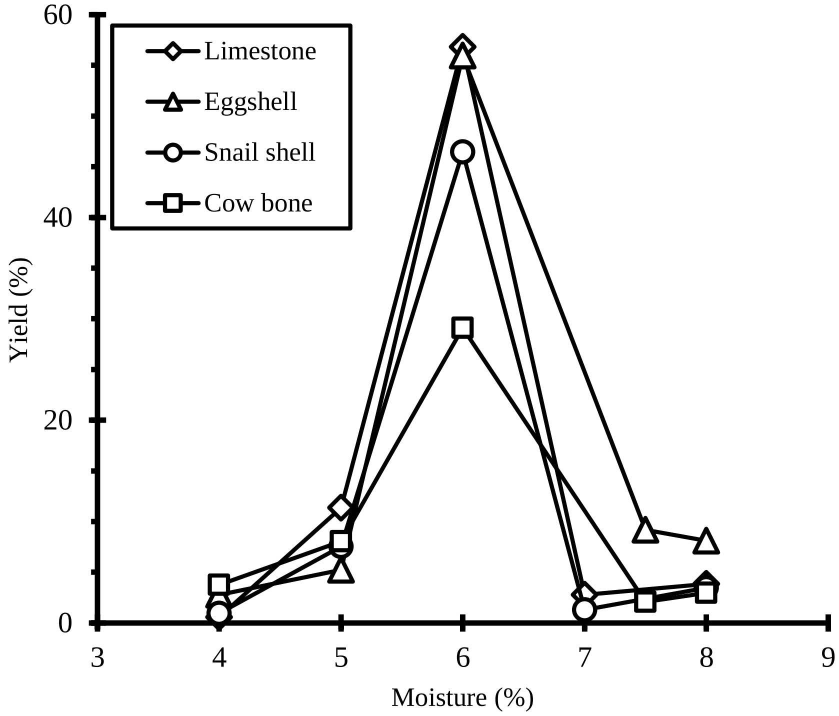


Fig. 4 Effect of moisture content on the yields of on-size NPK 15-15-15 granules

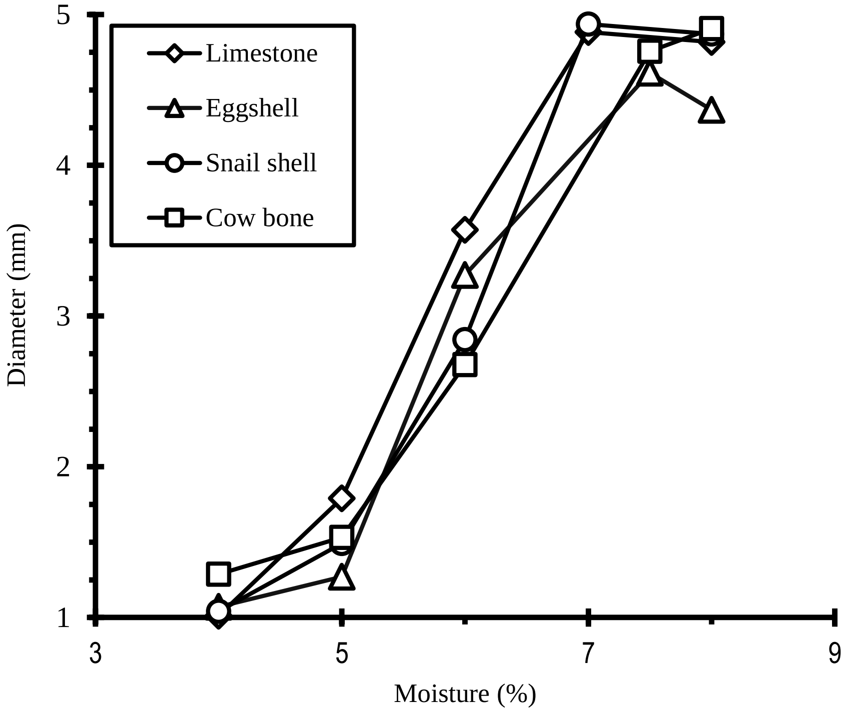


Fig. 5 Effect of moisture content on the average diameters of NPK 15-15-15 granules

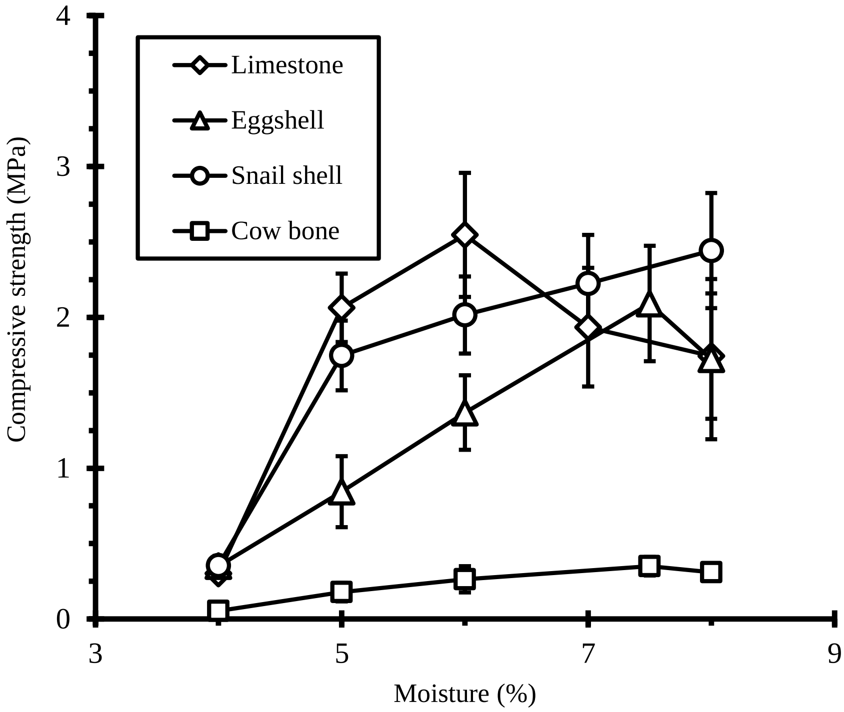


Fig. 6 Effect of moisture content on the strength of on-size NPK 15-15-15 granules

As shown in Fig. 6, the maximum strengths of NPK granules using eggshell, snail shell, and cow bone as fillers were found to be in the 7% to 8% moisture range. Compared to limestone, larger additional moistures were necessary to maximize the compressive strengths of NPK granules using eggshell, snail shell, and cow bone as fillers. The confidence intervals at 95% significance level for the maximum strengths achieved using limestone, eggshell, snail shell, and cow bone as fillers are (2.55±0.39), (2.09±0.36), (2.44±0.55), and (0.35±0.04) MPa, respectively. Comparative tests showed that the maximum strengths of granules using eggshell and snail shell as fillers were not significantly different from that using limestone as a filler. However, the maximum strength obtained using cow bone as a filler was significantly lower from that using limestone as a filler. Considering the maximum compressive strength of the on-size NPK granules that could be achieved, it could be said that the performance of fillers follows the order: limestone ≈ snail shell ≈ eggshell > cow bone.

From this comparative study, in view of yield and strength of on-size NPK granules obtained, eggshell and snail shell were found to be as good as limestone as fillers. However, cow bone is significantly worse than limestone. The low degree of granulation and the weakness of NPK granules were exhibited when using cow bone as a filler could be explained from its composition. Eggshells and snail shells, like limestone, are composed mainly of mineral, especially calcium carbonate, as shown by the spectra in Figs. 2 and 3. In contrast, cow bone contained a significant amount of organic matter, achieving 38.2%-w. In addition, it contained 17%-w fat. The presence of organic matter especially fat in high portion made cow bone more hydrophobic. The hydrophobicity can be represented by water drop penetration time of the mixed fertilizer-filler powders. With cow bone as fillers, the penetration time was found to be 5 minutes. While with other fillers, the penetration times were found to be less than 30 seconds. The binding solution is a water base, formed by the dissolution of soluble urea and KCl in the sprayed water. The more hydrophobic the powder, the weaker the interaction between the binder solution and particles. The hydrophobicity of cow bone also made the granulation of NPK powders with cow bone as fillers showed slower growth, as can be seen from the lower yield of on-size and higher yield of undersize granules for cow bone as filler at 6% additional moisture.

The results of this work indicated that fillers from agricultural wastes having high organic content or low mineral content tended to give poor granulation performance. It confirmed the previous findings.

Hardesty and Rose (1938) in studying granulation of fertilizer mixtures, most of which involving ammoniation, found that mixtures which consist largely of inorganic materials granulate more readily and with lower moisture than those relatively high in organic materials. Pesonen et al. (2016) who granulated sewage sludge from a municipal waste treatment plant and lime found that the higher the sewage sludge fraction, the weaker the granule obtained. The high mineral contents of eggshells and snail shells resulted in granular NPK fertilizers having on-size yield and compressive strength comparable to those with limestone as filler. These two solid agricultural wastes, therefore, can be considered as good alternatives for conventional fillers.

Figs. 7 and 8 illustrate the effects of formulas on the average diameter of granules and compressive strength of on-size granules, respectively, at 6% additional moisture. The results indicated that formula 20-10-10 gave higher granulation extent and higher compressive strength. As shown in Tables 2 and 3, formula 20-10-10 had higher urea content than formula 15-15-15. An increase in urea content which is readily soluble in water made granulation became more effective. Larger urea content, however, may give a problem with regard to granule stability due to the hygroscopicity of urea. The critical relative humidity of urea is 72.5% as a single component and is in the range of 60-62% when blended with DAP or KCl (Clayton 1984). To study the effect of formula on the stability of the NPK granules, about 8 to 10 grams of on-size granules were exposed to open air which was recorded to have relative humidity in the 80% to 82% range, that were above the critical humidity of urea. Fig. 9 presents the increase in weight measured at every hour of the on-size granules obtained at two formulas using snail shells as fillers at 6%-additional moisture. Although the differences are not large, the curves consistently showed that the 20-10-10 formula gained a greater weight than the 15-15-15 formula. This means that the 20-10-10 granules were more hygroscopic and more unstable than the 15-15-15 granules. Instability due to moisture absorption, however, was also shown by the NPK granules with limestone as filler, as can be seen in Fig. 9. In fact, instability due to hygroscopicity is an obvious problem. To prevent instability, hygroscopic fertilizers, especially urea-based fertilizers, are commonly coated before going to storage.

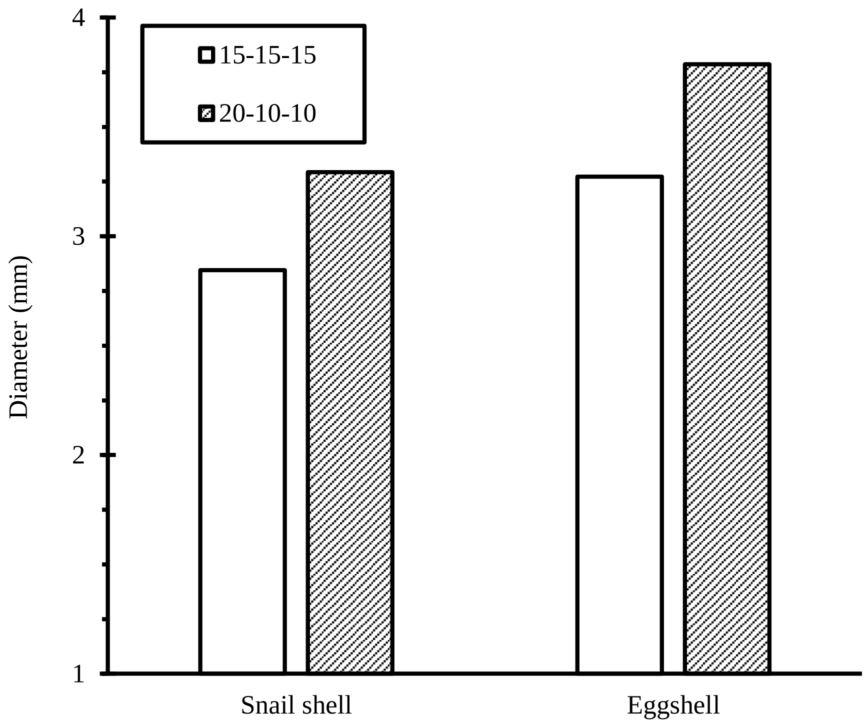


Fig. 7 Effects of formula on the average diameter of granules with snail shell and eggshell as fillers (6% additional moisture)

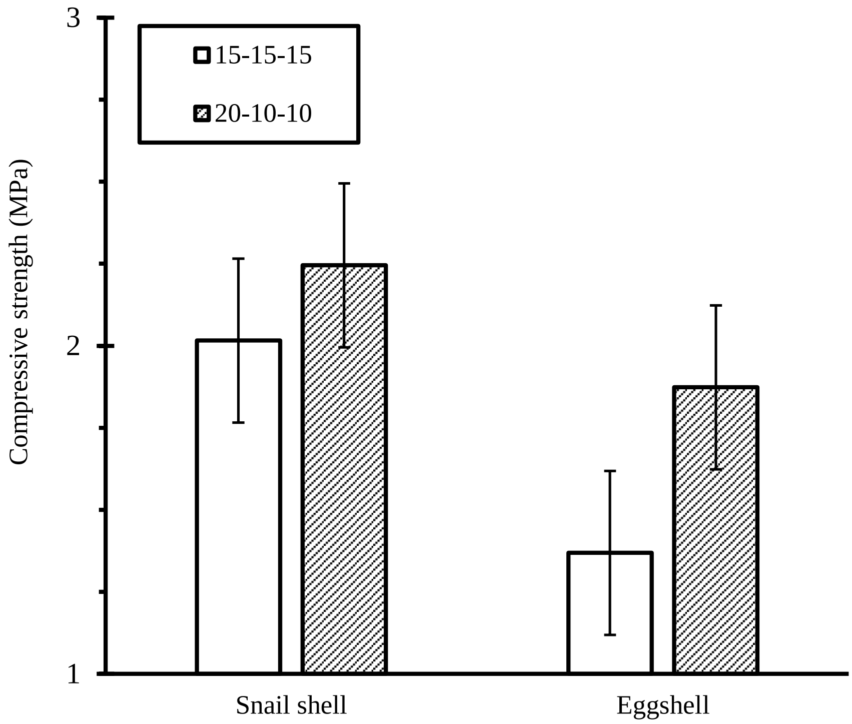


Fig. 8 Effects of formula on the compressive strength of on-size NPK granules with snail shell and eggshell as fillers (6% additional moisture)

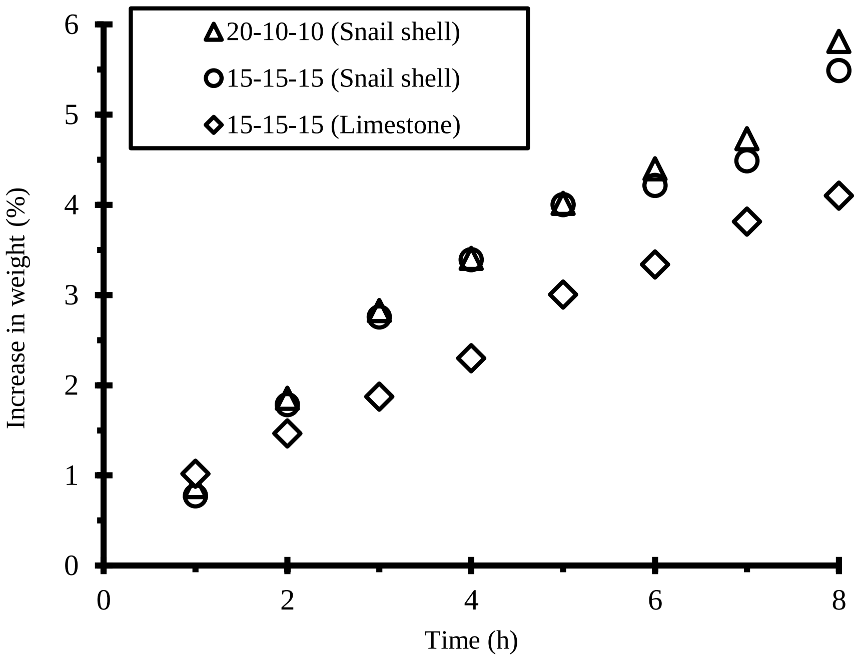


Fig. 9 The increasing weight of on-size NPK granules with time when exposing to open air (6% additional moisture, 80% relative humidity)

Analysis of plant nutrients

The nutrient contents of NPK granules from several runs were analyzed and presented in Table 4. The primary macro nutrient (N-P-K) contents required by both 15-15-15 and 20-10-10 formulas could be attained in ±1% deviations. The contents of calcium, a secondary macro nutrient, were also found to be close to the expected values. From material balances, the calcium contents in the NPK 15-15-15 granules were estimated to be 8.0%, 8.5%, 6.6%, and 7.8% for eggshell, snail shell, cow bone, and limestone as fillers, respectively. In the NPK 20-10-10 granules, they were estimated to be 9.8%, 10.4%, 8.1%, and 9.6% for eggshell, snail shell, cow bone, and limestone as fillers, respectively. The largest difference in calcium content between the measurement and the expected value is 1.2%, occurring in the NPK 20-10-10 with eggshell as a filler (#12). The results from samples #2, #3, and 4# which were obtained from replicated runs showed that the granulation gave consistent nutrient contents. The consistency of the nutrient contents in the on-size NPK granules with the targeted formulas confirmed that the three agricultural wastes studied here could mix well with all fertilizer components during the granulation. The results from samples #5, #6, and #7 showed that the targeted nutrient content could be achieved not only in the on-size but also in the undersize and oversize granules. Recycling both undersize and oversize fractions, as practiced in commercial productions, therefore, should not disturb the nutrient composition of granulator hold-ups.

The above discussion found that NPK granules produced using eggshells, snail shells, and cow bones as fillers have primary macro nutrient distributions as expected. Their distribution is as good as NPK granules with limestone as a conventional filler (#9). Considering the calcium contents, the peculiarity of limestone as a calcium source for plant is also retained by the studied agricultural wastes. Moreover, the calcium contained in the NPK granules obtained using the agricultural wastes as fillers are renewable. This will become beneficial in using agricultural wastes as fillers in view of sustainability compared to limestone that supplies unrenewable calcium. Considering also the results of the comparison on yield and strength of on-size granules, which showed that cow bone resulted in weak granules, it could be said that among the three alternative materials studied, eggshells and snail shells are as good as limestone to be used as filler in making granular NPK fertilizer by physical granulation.

Table 4 Nutrition analysis of granules

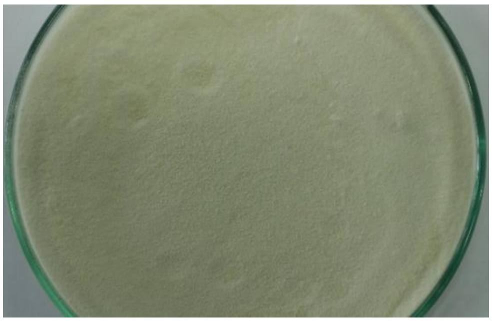
#	Filler	Moist	Fraction	N	P[1)]	K[2)]	Ca
	Formula: 15-15-15						
1	Snail shell	6%	on-size	13.6	15.8	15.9	8.3
2	Egg shell	6%	on-size	15.2	15.6	14.9	8.4
3	Egg shell	6%	on-size	14.9	15.7	14.5	7.9
4	Egg shell	6%	on-size	14.7	15.7	14.8	8.2
5	Egg shell	7%	undersize	14.4	15.7	14.2	7.9
6	Egg shell	7%	on-size	15.1	15.7	14.5	8.3
7	Egg shell	7%	oversize	15.4	15.2	15.2	8.6
8	Cow bone	7%	on-size	14.6	16.6	15.4	7.4
9	Lime stone	6%	on-size	15.2	16.0	15.3	8.3
	Formula: 20-10-10						
10	Snail shell	4%	on-size	19.2	10.6	10.0	10.6
11	Snail shell	6%	on-size	19.7	10.6	10.5	10.8
12	Egg shell	7%	on-size	20.0	10.3	9.6	11.0

[1)]as P_2O_5. [2)]as K_2O

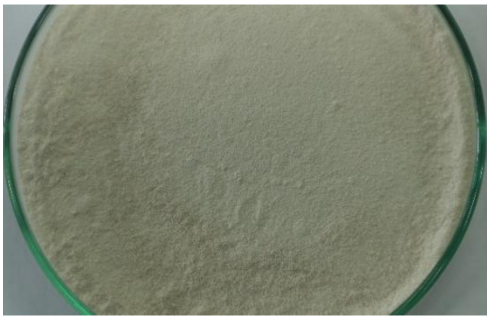
Granule Appearance

Fig. 10 shows the photographs of raw material powders. The urea, DAP, and KCl used were white, greenish-white, and pale pink, respectively. Snail shell and eggshell powders had a color close to that of limestone. Cow bone powder had a dark yellow color. The photographs of NPK granules are presented in Fig. 11. Most NPK granules obtained were spherical. It could be seen that the colors of NPK granules were influenced by the fillers. It is reasonable as filler contributed a significant amount in the NPK formulas (21 to 29%-w in NPK 15-15-15). Granules with snail shells and eggshells as fillers had almost similar colors, i.e. cream color, to those with limestone as fillers. Cow bones gave NPK granules having pale yellow. Using eggshells, snail shells, and cow bones as fillers, therefore, physical granulation produces granular NPK fertilizers with colors from a cream color to a pale yellow. These colors of NPK granules may not have a special appeal for the market. On the other hand, it became a question whether the NPK granules produced with the cream color to pale yellow will make the granules rejected by the market. Granular NPK fertilizers in the market are supplied in various colors, white, red, yellow, blue, green, pink, or black. Since the market has accepted many colors, NPK granular fertilizers with cream color to pale yellow obtained using the agricultural wastes as fillers are most likely to be accepted by the market.


Urea


DAP


KCl

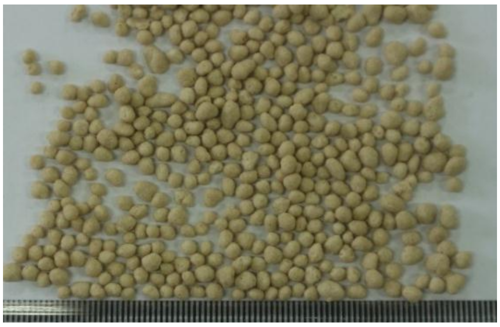

Snail shell


Egg shell

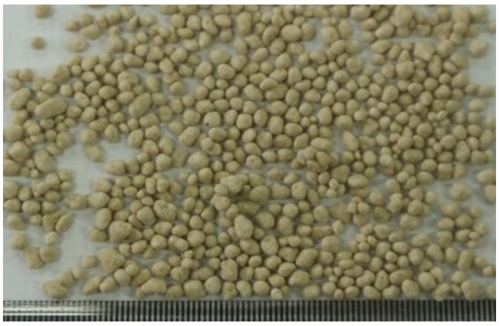

Cow bone


Lime stone

Fig. 10 Photographs of fertilizer and filler powders



Egg shell as filler



Snail shell as filler

Cow bone as filler

Lime stone as filler

Fig. 11 Photographs of NPK 15-15-15 granules with various fillers

Conclusion

NPK fertilizer granules made by physical granulation of urea, DAP, KCl, and agricultural wastes (snail shells, eggshells, and cow bones) as fillers on a disc granulator have been evaluated and compared to limestone as a conventional filler. Snail shells and eggshells as fillers gave on-size (2 to 4 mm) NPK granules having yield and strength which were comparable to those with the conventional filler. For NPK 15-15-15, on-size granules with 46% and 56% yields could be obtained using snail shells and eggshells as fillers, respectively. The compressive strengths of on-size granules could achieve 2.4 and 2.1 MPa, respectively. Cow bones as fillers, however, resulted in significantly weaker NPK granules compared to the conventional filler. The distribution of nutrients in the NPK granules was found to be close to the targeted formula. The effects of additional moisture on the yield and strength of on-size granules using agricultural wastes and limestone as fillers were found to have the same trends.

Acknowledgements This research was supported by Institut Teknologi Bandung under the Grant Research, Community Service, and Innovation 2018. We express our thanks to P.T. Petrokimia Gresik for providing DAP fertilizer and to P.T. Pupuk Kujang for nutrient analysis.

Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study.

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