Biopellet properties of agathis wood fortified with its peeled-off bark

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Abstract. The agathis bark is expected to increase the energy content and durability of the resulting biopellet. The present research was aimed to analyze chemical components of agathis and to determine the quality of agathis wood biopellet fortified with it loosen bark. The klason lignin, extractives, holocellulose and α-cellulose content of wood and bark of the agathis were determined following the standard procedures of TAPPI T 222 0m-88, TAPPI T 204 0m-88, and Browning (1967), respectively. Biopellets of 15 mm diameter were prepared with pelletizing pressure of 1500 psi. The moisture content, ash content, density, durability, and calorific value of the resulting biopellet were compared to those required by DIN EN 14961-2 and 51731 standards. The α-cellulose and holocellulose content of the agathis bark were found lower than these of its wood. However, its klason lignin, extractive, and ash content were higher than these of its wood. The resulting biopellet retained the density of 0.61-0.71 g/cm³, moisture content of 0.42-4.52%, ash content of 0.79-2.73%, durability of 21.26-44.59%, and calorific value of 4,524-4,628 kcal/kg. Except for that of the biopellet density and durability, all parameters satisfied the requirements of DIN EN standards. Thermal analysis of biopellet showed that water loss occurred at 36-100°C and significant mass decomposition between 100 up to 475°C with the weight loss of 77.34-80.51%. No further decomposition was found at above 480°C.

1. Introduction
The reserve of fossil-based energy such as petroleum, natural gas, and coal were predicted will last only for 40, 60, and 200 years to come, respectively [1]. Therefore, the search for fossil fuel alternatives is paramount. Biomass could be the most appropriate source for a renewable and environmentally friendly energy of the future. Biomass based energy is considered free of green house gases and CO₂ emission [2,3]. Its renewable nature will ascertain the sustainability of energy reserve.

In the 2012, consumption of biomass-based fuels in Indonesia was about 56.12 million tones, which was higher than that of coal with about 28.97 million tones [4]. The source of biomass energy can be from wood, kenaf, bamboo, and the waste of sawmill, forest industries, agriculture, paper products, sugar cane, and other lignocellulosic materials [5].

Biomass can be converted into gas, liquid and solid bio-fuels. The most common form of solid bio-fuel are briquette, biopellet, and cubes. Biopellet, which is prepared by pelletizing wood meals, is gaining popularity mainly in the European countries [6]. Biopellet demand in Sweden for instance, increased to 240% from 1997 to 2006 with a 45% increase in its price [7].
Wood is the most abundant terrestrial biomass. Agathis wood, for example, is a versatile biomass widely cultivated in Indonesia. It is used for raw material of woodworking, fuel-wood and its resin is tapped for various derivative non-wood forest products. Production of agathis wood in 2010-2011 just by Perum Perhutani, a state own enterprise, was of 305.728 m$^3$ [8]. In general, trees consist of about 10-20% bark [9], thus upon harvesting, Perum Perhutani wastes approximately of 30.573-61.146 m$^3$ wood bark. Furthermore, agathis wood produces a naturally peeled off bark that thicken when it’s growing to maturity. Bark is rich in lignin and extractives that relatively higher in energy content compared to that of polysaccharide. Lignin and extractives content of agathis wood were reported to the amount of 24.7% and 2.0%, respectively, with calorific value of 4,762 kcal/kg [10].

It is a common knowledge that the energy density of wood is relatively low compared to coal or charcoal. Considering that the relatively high content of lignin and extractives in the bark, agathis bark could be also used to fortify its wood in the production of biopellet. The use of bark could also result in a durable biopellet. Bark fortified Scott pine biopellet was reported to reach a durability of 95-97% [11].

Even though the quality requirement of biopellet varied according to different standards, however, they all are dependent on its moisture content, ash content, durability, and calorific value. Biopellet durability is important during its transportation. Densification pre-heating, moisture content, raw material, particle size, peletizing pressure, peletizing temperature, peletizing time, and biopellet diameter [12,13] influence the durability of biopellet. Particle size determines biopellet density, combustion period, and durability [13,14]. Smaller particle tends to increase density and combustion time [15]. Biopellet produced from particle size of less than 1.4 mm resulted in a higher durability compared to that produced from particle size of 1.4-3.2 mm [13]. In the present works, smaller particle size of agathis bark was used with an expectation of increasing biopellet density and durability. Despite the fact that its high lignin content is beneficial for pellet durability and calorific value, the use of bark in biopellet production tends to increase its ash content [11]. The high ash content of biopellet will bring about the formation of crust in combustion chamber (furnace). Currently, in order to cultivate the beneficial effect (calorific value and durability) of using bark, the percentage of bark used was varied to the maximum of 30%.

The present research was intended to determine the quality of agathis wood biopellet fortified with its peeled-off barks densified at various temperature. Thermal behavior of agathis wood peeled-off bark and its biopellet was also analized.

2. Materials and Methods

2.1. Materials

A 50 years old agathis wood was chipped and air-dried. The moisture content of the air-dried chips was then determined. The moisture content of biopellet raw material should be approximately at 8-12%. The chips were milled and sieved to obtain wood meal of 20-40 mesh (0.84-0.42 mm) for biopellet production and 40-60 mesh (0.42-0.25 mm) for chemical and proximate analysis. Figure 1 indicates general outline of the present research.

Biopellet was prepared by thoroughly mixing the wood meal (W) and bark meal (B) based on their oven dry weight. The compositions (% B/W) of biopellet were varied at 0/100, 10/90, 20/80, and 30/70 referring to Filbakk et al. [11] which used pinewood.
2.2. Methods

2.2.1. Chemicals and proximate analysis
The chemical contents of wood and bark were determined in accordance with TAPPI [16] T 204 om-88 (EtOH-Benzene extractives), TAPPI T 222 om-88 (Klason lignin), and Browning (1967) for \( \alpha \)-cellulose and hemicellulose content. Proximate analysis was done following the ASTM E-871 [17] for the determination of moisture content, and ASTM D-1102 [18] for the determination of ash content, volatile content, and fixed carbon.

2.2.2. The preparation of biopellet
Biopellets with a diameter of 15 mm were prepared in a pelletizer using pelleting pressure of 10.34 MPa. Pelletizing temperature varied at 130, 160, and 190°C following those applied previously by Lee et al. [13] Pelletizing process was carried out for 6 min consisting of 3 min pre-heating and 3 min of heating at the predetermined pelleting temperatures. Upon pelletizing, the biopellets were conditioned for one day before the determination of the biopellets moisture content, density, ash content, durability, and the calorific value. TG-DTA of the raw materials (wood and bark) and selected biopellet (biopellet with bark content of 30%) was also conducted to evaluate their thermal behavior.

2.2.3. The measurement of biopellet quality

2.2.3.1. Moisture content
Moisture content was calculated as a ratio between moisture weight in a sample and oven dry weight of the biopellet. Oven dry weight of biopellet was procured by oven drying at 103±2°C to a constant weight. DIN EN 14961-2 [19] requires the biopellets moisture content of 10%. The moisture content was calculated by the following formulae:

\[
\text{Moisture Content (\%)} = \frac{\text{Green weight (g)} - \text{Oven dried weight (g)}}{\text{Oven dried weight (g)}} \times 100
\]  

(1)

2.2.3.2. Density
The density of biopellet was determined in accordance with the standard of DIN EN 51731 [20], which requires the biopellets density of 1.00-1.40 g/cm³. The density of biopellet was calculated by the following formulae:
Density (g/cm$^3$) = \frac{\text{The weight of biopellet (g)}}{\text{The volume of biopellet (cm$^3$)}} \quad (2)

2.2.3.3. Ash content
Ash content (in percent) is the residue of sample combustion at 600°C for 4 hours expressed as percentage. DIN EN 14961-2 [19] requires the ash content of less than or equal to 3%. The ash content was calculated by the following formulae:

\text{Ash content (%)} = \frac{\text{The weight of ash (g)}}{\text{Oven dry weight of sample (g)}} \times 100 \quad (3)

2.2.3.4. Durability
A durability tester was used to determine the durability of the biopellet. In which, 100 g of biopellet were shaken at 50 rpm for 10 min. Upon shaking, the biopellets were sieved in a 20 mesh screen. The biopellets remained on the 20 mesh screen were then weighed. DIN EN 14961-2 [19] requires the minimum durability of 96.5%. The durability of the biopellet was calculated following the formulae of:

\text{Durability (%)} = \frac{\text{The weight of biopellet retained on 20 mesh sieve (g)}}{100 (g)} \times 100 \quad (4)

2.2.3.5. The caloric value
Bomb Calorimeter Parr 6400 was used to determine the caloric value of the biopellet. The analysis was involving the use of oxygen (450 psi), nitrogen (80 psi) and benzoic acid. The caloric value of the biopellets was calculated following the formulae of:

\text{Calorific value (kcal/kg)} = \frac{Wt - e1 - e2 - e3}{m} \quad (5)

where: \( W \) = equivalent energy value of benzoic acid \\
\( t \) = temperature increase differential (°C) \\
\( e1 \) = chrom nickel wire correction \\
\( e2 \) = sulphur correction \\
\( e3 \) = nitric acid correction \\
\( m \) = sample mass (gram)

2.2.4. Thermal analysis
Thermographimetric analysis (TGA) and differential thermal analysis (DTA) using Thermal Gravimetric/ Differential Thermal Analyzer (TG/DTA) SII EXSTAR 7300 (Hitachi High-Tech Science Corporation, Tokyo) were carried out to analyze the thermal behavior of the biopellet and its raw materials. Approximately 3-5 mg of sample was put in the sample container made of Alumina/Pt, and the analysis was done with the air flow rate of 50 cm$^3$/min and the heating rate of 10°C/min until the temperature of 1200°C.

2.3. Data analysis
Data were analyzed using a factorial completely randomized design with 3 factors, i.e. particle size (A) with 2 levels (20-40 mesh and 40-60 mesh), percentage of peeled off bark (B) with 5 levels (0, 10, 20, 30, and 100% of bark content), and pelleting temperature (C) with 3 levels (130, 160, and 190°C). All experimentation was done in three replicates. The general model of the design used to analyze the quality of biopellet such as density, moisture content, ash content, and durability was:

\[ Y_{ijk} = \mu + A_i + B_j + C_k + (AB)_{ij} + (AC)_{ik} + (BC)_{jk} + (ABC)_{ijk} + \varepsilon_{ijk} \quad (6) \]
where:

\[ Y_{ijk} \]: the score of the ith factor A (particle size), the jth factor B (percentage of peeled-off bark), and the kth factor C (peletizing temperature)

\[ \mu \]: the overall population mean

\[ A_i \]: effect of ith level of A

\[ B_j \]: effect of jth level of B

\[ C_k \]: effect of kth level of C

\[ (AB)_{ij} \]: joint effect of the ith level of A and the jth level of B

\[ (AC)_{ik} \]: joint effect of the ith level of A and the kth level of C

\[ (BC)_{jk} \]: joint effect of the jth level of B and the kth level of C

\[ \varepsilon_{ijk} \]: the error effect associated with \( Y_{ijk} \)

Calorific value was analyzed with completely randomized factorial design with one factor A (the percentage of peeled-off bark in biopellet) at four levels (0, 10, 20, 30, and 100 %). The general model used was:

\[ Y_i = \mu + B_i + \varepsilon_i \]  

where:

\[ Y_i \]: the score of the ith level factor A (the percentage of peeled-off bark)

\[ \mu \]: mean value

\[ B_i \]: effect of the ith level factor A

\[ \varepsilon_i \]: the error associated with \( Y_i \)

P-value was used as the test criteria. P-value \( \leq 0.05 \) indicates that the effect of treatment is significant at the level of confidence of 95% and P-value \( > 0.05 \) indicates that the effect of treatments is insignificant at the level of confidence of 95%. Duncan’s multiple range test was carried out to evaluate the differences among treatments.

3. Results and Discussion

3.1. Chemical components of agathis wood

The content and types of the chemical components of wood influence its energy characteristics. Table 1 indicates the chemical compositions and proximate analysis of agathis wood and its bark. It can be seen (from Table 1) that Klason lignin, extractives, and fixed carbon of the bark are higher than those of wood are. The Klason lignin and extractives content of the peeled-off bark of agathis is higher than the lignin and extractives content found in the bark of Pinus sylvestris and Picea abies by Miranda et al. [21] that was 26.8-32.9 % and 5.0-5.3%, respectively.

Carbon content of biomass determines its calorific value, in which increasing carbon content tends to increase the calorific value. Lignin is a phenolic compound consist of phenylpropane units with a relatively high content of carbon. Extractives such as wax, protein, sugar, pectin, resin, terpene, starches, and saponin are also carbaneous compound [22]. Ma et al. [23] reported that the carbon content of lignin, cellulose, and non-structural cellulose was 63-66%, 44%, and 44%, respectively. Therefore, calorific value of lignin and extractives is commonly higher than that of cellulose and hemicellulose. The calorific value of cellulose, lignin and extractives is of 4150-4350 kcal/kg, 6100 kcal/kg dan 8500 kcal/kg, respectively [24]. Based on the content of its lignin, extractives, and fixed carbon, the peeled-off bark of agathis should be a good fortifier for increasing the calorific value of its wood biopellet. However, the benefit of higher lignin content of the bark to the calorific value of biopellet could be counterweighed by its higher ash and moisture content. Ash and moisture content adversely influence the calorific value of biomass.
Table 1. Chemical components and proximate analysis of the peeled-off bark and wood of agathis

| No. | Components* | Unit | Bark (B) | Wood (W) |
|-----|-------------|------|----------|----------|
| 1   | Extractives | %    | 12.47    | 6.65     |
| 2   | Klason Lignin| %    | 42.64    | 30.94    |
| 3   | Holocellulose| %    | 54.53    | 71.06    |
| 4   | α-cellulose | %    | 32.54    | 49.80    |
| 5   | Hemicellulose| %    | 21.99    | 21.26    |

Proximate analysis

| No. | Components    | Unit | Bark (B) | Wood (W) |
|-----|---------------|------|----------|----------|
| 6   | Ash content   | %    | 2.63     | 1.08     |
| 7   | Moisture content| %    | 13.29    | 11.73    |
| 8   | Volatile Content| %    | 68.13    | 78.79    |
| 9   | Fixed Carbon  | %    | 30.79    | 18.58    |

note: (*) the values are the average of three replicates

3.2. The quality of biopellet

3.2.1. Moisture content

Moisture content is an important determining quality of biopellet due to its direct relation with calorific value. Table 2 indicates that biopellet with the highest moisture content was found on the biopellet produced from bark with 40 mesh particle size and peletized at 130°C, while the lowest was from biopellet prepared from wood with particle size of 60 mesh peletized at 190°C. All biopellet fulfilled the DIN EN 14961-2 [19] standard that require the moisture content of equal or less than 10%.

Analysis of variance (Table 3) indicates that particle size, bark content, pelletizing temperature and all interaction of factors significantly influenced the biopellet moisture content. Further evaluation using mean range test of Duncan indicates that the moisture content of biopellet produced from raw material with particle size of 60 mesh, 20% bark content and pelletized at 130°C was significantly lower than that produce with the same particle size and bark content, but pelletized at 160°C and 190°C. The moisture content of biopellet with 160°C and 190°C pelletizing temperature was insignificantly different. Therefore, biopellet produced from particle size of 60 mesh, 20% bark content and pelletized at 130°C is the most acceptable in term of moisture content, despite all pelleting temperature applied fulfilled the DIN EN 14961-2 [19] standard requirement. It seemed that producing biopellet with smaller particle size and pelletizing at higher temperature tended to lower the moisture content. The moisture content of biopellet prepared from teak, acacia and sengon wood also decreased with increasing pelleting temperature [14].

3.2.2. Density

Biomass is bulky and relatively low in energy content base on its volume. These properties bring about the biomass transportation and storage is inefficient. Densification or pelletizing will increase the density and the energy content of biomass. The density of biomass influences the density of the resulting biopellet. The density of agathis wood is in the range of 0.47-0.48 g/cm³ [10]. In the present works, the density of the produced biopellet was of 0.61-0.71 g/cm³. It is far below the DIN EN 51731 standard [20] requirement of 1.00-1.40 g/cm³.

The influence of particle size, bark content, pelletizing temperature and interaction of factors can be seen in Table 3. The effect of bark content on the density of biopellet reported by several researchers is opposing, somehow. The present research indicates that bark tended to increase biopellet density; however, Filbak et al. [11] found that bark insignificantly influenced the density of pine wood biopellet. The highest density of biopellet was resulted from biopellet made of 100% bark with particle size of 60 mesh pelletized at 160°C, and the lowest density was resulted from biopellet made of 100% bark with
particle size of 40 mesh pelletized at 130°C. Higher lignin content of bark and higher surface area of smaller particle size could be the origin of this occurrence. Duncan MRT indicated that the biopellet density using 20% and 30% bark content with particle size of 60 mesh pelletized at 130°C was insignificantly different. Therefore, considering the relatively limited amount of bark, using 20% bark as fortifier is more efficient than that using 30% bark. Furthermore, using lower pelletizing temperature will be less costly in term of energy input during biopellet production processes. Refining process and pelletizing at high temperature are the most energy consuming in the production of biopellet. Data in Table 3 also indicates that temperature in interaction with bark content and particle size tends to be more influential on the density of biopellet at higher bark content.

### Table 2. Quality parameters of the currently produced biopellet

| Treatments | Particle size (Mesh) | Bark content (%) | Pelletizing temperature (°C) | Moisture content (%)* | Density (g/cm³)* | Ash content (%)* | Durability (%)* |
|------------|----------------------|------------------|------------------------------|-----------------------|-----------------|-----------------|-----------------|
| B0         | 130                  | 3.59±0.31        | 0.64±0.03                   | 0.82±0.10             | 26.10±1.07      |
|            | 160                  | 2.19±0.05        | 0.65±0.01                   | 0.79±0.07             | 21.26±0.83      |
|            | 190                  | 1.34±0.19        | 0.61±0.02                   | 0.82±0.02             | 24.65±0.28      |
| B10        | 130                  | 3.40±0.02        | 0.64±0.02                   | 0.79±0.09             | 30.22±0.62      |
|            | 160                  | 1.93±0.21        | 0.67±0.01                   | 1.19±0.14             | 22.17±1.22      |
|            | 190                  | 1.16±0.16        | 0.68±0.02                   | 0.99±0.16             | 25.57±1.17      |
| B20        | 130                  | 3.00±0.28        | 0.61±0.02                   | 1.11±0.19             | 34.29±0.92      |
|            | 160                  | 2.65±0.19        | 0.61±0.01                   | 1.03±0.07             | 26.37±1.06      |
|            | 190                  | 2.11±0.09        | 0.63±0.01                   | 1.36±0.15             | 30.01±1.06      |
| B30        | 130                  | 3.96±0.34        | 0.69±0.04                   | 1.48±0.09             | 35.87±1.63      |
|            | 160                  | 3.30±0.24        | 0.62±0.01                   | 1.50±0.07             | 26.26±0.79      |
|            | 190                  | 1.32±0.27        | 0.65±0.02                   | 1.42±0.09             | 31.60±1.10      |
| B100       | 130                  | 4.52±0.20        | 0.61±0.00                   | 2.48±0.05             | 30.54±0.74      |
|            | 160                  | 2.57±0.29        | 0.63±0.03                   | 2.58±0.04             | 25.65±0.64      |
|            | 190                  | 1.57±0.17        | 0.65±0.02                   | 2.73±0.06             | 29.65±0.56      |
| B0         | 130                  | 1.43±0.31        | 0.67±0.03                   | 1.21±0.09             | 36.31±0.92      |
|            | 160                  | 1.13±0.24        | 0.63±0.00                   | 1.11±0.12             | 26.28±0.75      |
|            | 190                  | 0.42±0.14        | 0.68±0.02                   | 1.03±0.14             | 33.62±1.07      |
| B10        | 130                  | 1.45±0.13        | 0.64±0.02                   | 1.22±0.04             | 40.39±0.85      |
|            | 160                  | 0.77±0.16        | 0.65±0.02                   | 1.24±0.07             | 27.80±0.58      |
|            | 190                  | 0.42±0.21        | 0.68±0.02                   | 1.45±0.17             | 36.44±1.07      |
| B20        | 130                  | 1.44±0.30        | 0.64±0.03                   | 1.43±0.08             | 44.12±1.39      |
|            | 160                  | 0.63±0.07        | 0.62±0.01                   | 1.44±0.14             | 31.25±1.47      |
|            | 190                  | 0.55±0.31        | 0.65±0.04                   | 1.46±0.06             | 41.38±0.83      |
| B30        | 130                  | 2.31±0.16        | 0.63±0.03                   | 1.79±0.06             | 44.59±0.54      |
|            | 160                  | 1.02±0.12        | 0.66±0.02                   | 1.65±0.01             | 38.91±1.01      |
|            | 190                  | 0.56±0.03        | 0.62±0.01                   | 1.64±0.17             | 42.54±0.78      |
| B100       | 130                  | 3.25±0.24        | 0.66±0.01                   | 2.25±0.05             | 34.33±0.74      |
|            | 160                  | 1.39±0.26        | 0.71±0.02                   | 2.48±0.08             | 40.84±0.86      |
|            | 190                  | 0.90±0.29        | 0.70±0.03                   | 2.50±0.06             | 39.63±0.53      |

Note: (*) the average of tree replicates

Table 3 shows that the R-squared for biopellet density is 69%. This implies that in addition to particle size, bark content, and pelletizing temperature, other factors (at the level of 31%) also influenced the density of the biopellet. Pelletizing pressure is an important influencing factor that determines biopellet...
density. In the current works, pelleting pressure used was considered low, i.e. at 10.3 MPa as compared to optimum pressure of 100-150 MPa according to Kaliyan and Morey [12].

Table 3: Analysis of variance of the biopellet quality parameters

| Components                  | Moisture content | Density | Ash content | Durability |
|-----------------------------|------------------|---------|-------------|------------|
| R-squared                   | 0.97             | 0.69    | 0.98        | 0.99       |
| RMSE                        | 0.21             | 0.02    | 0.10        | 0.98       |

Effect Test (P-Values)

|                               |                 |         |             |            |
|-------------------------------|-----------------|---------|-------------|------------|
| Particle size (A)              | < 0.0001        | 0.0006  | < 0.0001    | < 0.0001   |
| Bark content (B)               | < 0.0001        | 0.0003  | < 0.0001    | < 0.0001   |
| Pelletizing temperature (C)    | < 0.0001        | 0.1915  | 0.1327      | < 0.0001   |
| A * B                         | 0.0001          | < 0.0001| < 0.0001    | 0.0006     |
| A * C                         | < 0.0001        | 0.6028  | 0.0089      | < 0.0001   |
| B * C                         | < 0.0001        | 0.0024  | 0.0006      | < 0.0001   |
| A * B * C                     | < 0.0001        | 0.0008  | 0.0071      | < 0.0001   |

Note: P-Value ≤ 0.05 significantly different and P-Value > 0.05 insignificantly different at confidence level of 95%.

3.2.3. Ash content

Ash reduces the quality of biopellet. The ash content of the presently produced biopellet was in the range of 0.79 - 2.73% (Table 2), well below the requirement of DIN EN 14961-2 standard [19] that requires an ash content of less than 3%. The ash content was mainly influenced by the bark content used in the preparation of the biopellet. Increasing bark content increased the ash content of the resulted biopellet. Using a 100% bark to produce biopellet increased ash content nearly to the same level of the ash content of bark (2.7%). The relatively low ash content of the presently produced biopellet could be a new source of renewable and environmentally friendly solid fuel. It is a better solid fuel compared to coal-based fuel [2], where coal combustion emits 18.1 - 19.2% ash of its weight [25].

Analysis of variance (Table 3) indicates that pelleting temperature insignificantly influenced the ash content of biopellet. Biopellet with 30% bark content made of 60 mesh particle size at pelleting temperature of 130 °C was higher than that with 20% bark content prepared under similar particle size and pelleting temperature. Therefore, using 20 bark content will be a better choice in preparing biopellet from agathis wood. Refining the raw material to a higher degree also significantly increased the ash content. Biopellet made from particle size of 60 resulted in a higher biopellet ash content compared to that of biopellet made from particle size of 40. Similar results were reported by Miranda et al. [21] in the production of biopellet with Pinus sylvestris and Picea abies woods. These authors concluded that ash is biopellet commonly related to the presence of nitrogen, kalsium and potasium in the raw materials.

3.2.4. Durability

Durability is indicative of the biopellet resistance to an external impact during transportation process. Biopellet durability is very important in storage and for long distance transportation. The durability of the presently produced biopellet was in the range of 21.26 - 44.59% (Table 2), which was far below the requirement of DIN EN 14961-2 standard [19] that required the durability of 96.5% or higher. Biopellet durability is related to pelleting pressure and density. A 10.34 MPa pressure used in the present works brought about a low density and consequently low biopellet durability. The pelleting pressure used was assumed inadequate to form a good interparticle bonding in the biopellet.

Table 3 shows that particle size, bark content, pelleting temperature, and interaction of factors significantly influenced the durability of biopellet. The durability of biopellet prepared with 60 mesh particle size was higher than that prepared from particle size of 40 mesh, which is in accordance with
the previous finding of Lee et al. [13]. Higher durability of biopellet produced with 60 mesh particle size is possibly caused by the higher surface area of the finer particle that enable the particle to form a better interparticle bonding. Biopellet with 20% bark content pelletized at 130°C is the most preferable in term of its durability. The glass transition (Tg) temperature of lignin is slightly varied among lignocellulosic materials. The Tg of eucalypt and pinewoods for instant was found in the range of 120-140°C [26]. Pelletizing at 130°C might be the right temperature to melt lignin without degrading its polymer structure, thus it forms a good adhesive for interparticle bonding. Possible degradation of lignin structure at higher pelletizing temperature could be the origin of the reduced biopellet durability.

| Treatments | Particle size | Bark content | Pelletizing temperature | Moisture content | Density | Ash content | Durability |
|------------|--------------|--------------|-------------------------|------------------|---------|-------------|------------|
| B0         | 130          | C            | CDEFGH                  | KL               | LM      |
|            | 160          | GH           | CDEFGH                  | L                | O       |
|            | 190          | JK           | H                       | KL               | M       |
| B10        | 130          | C            | DEFGH                   | L                | JK      |
|            | 160          | H            | ABCDE                   | GHI              | N       |
|            | 190          | JK           | ABC                    | JK               | M       |
| B20        | 130          | DE           | GH                      | HIJ              | G       |
|            | 160          | EF           | GH                      | IJ               | LM      |
|            | 190          | GH           | EFGH                    | FG               | JK      |
| B30        | 130          | B            | AB                      | DEF              | GH      |
|            | 160          | CD           | GH                      | DEF              | LM      |
|            | 190          | IJK          | CDEFGH                  | F                | J       |
| B100       | 130          | A            | H                       | B                | JK      |
|            | 160          | F            | EFGH                    | AB               | M       |
|            | 190          | I            | CDEFGH                  | A                | K       |
| B0         | 130          | IJ           | ABCDE                   | GH               | G       |
|            | 160          | JKL          | DEFGH                   | HIJ              | LM      |
|            | 190          | O            | ABCD                    | IJ               | I       |
| B10        | 130          | IJ           | CDEFGH                  | GH               | DEF     |
|            | 160          | MNO          | CDEFGH                  | GH               | L       |
|            | 190          | O            | ABC                     | F                | G       |
| B20        | 130          | IJ           | CDEFGH                  | F                | AB      |
|            | 160          | NO           | FGH                     | F                | JK      |
|            | 190          | NO           | CDEFGH                  | EF               | CD      |
| B30        | 130          | FG           | EFGH                    | C                | A       |
|            | 160          | KLM          | BCDEFG                  | CD               | F       |
|            | 190          | NO           | GH                      | CDE              | BC      |
| B100       | 130          | CD           | ABCDE                   | B                | HI      |
|            | 160          | IJK          | A                       | B                | DE      |
|            | 190          | LMN          | A                       | B                | EF      |

Note: the same letter indicates an insignificantly different; different letter indicates a significantly different

3.2.5. The calorific value

Calorific value is the main factor to be considered for the use of biomass as the source of fuel. In order to evaluate the highest possible calorific value of the present experiments, the measurement of the calorific value was carried out for the biopellet prepared with 60 mesh particle size pelletized at 190°C. At this pelletizing temperature, the moisture content of biopellet was the lowest. The calorific value of
the tested samples was in the range of 4,524-4,628 kkal/kg (Table 5) that satisfied the requirement of DIN EN 14961-2 standard [19] of 3,821-4,538 kkal/kg. Table 5 shows that agathis wood biopellet with an acceptable calorific value can be produced by the addition of 10-30 % bark, particle size of 60 mesh, and pelleting temperature of 190°C. Even though a very high calorific value can be acquired by preparing biopellet purely with bark, the availability of the bark would prevent the sustainability of the biopellet production.

Table 5. Calorific value of biopellet prepared from 60 mesh particle size and pelleting temperature at 190°C.

| No | Bark content | Calorific value (kkal/kg) * | Duncan MRT** |
|----|--------------|-----------------------------|--------------|
| 1  | B0           | 4524±54                     | C            |
| 2  | B10          | 4566±17                     | BC           |
| 3  | B20          | 4578±07                     | AB           |
| 4  | B30          | 4616±19                     | AB           |
| 5  | B100         | 4628±07                     | A            |

Note: (*) average of tree replicates; (**) the same letter indicates insignificantly different and different letter indicates a significantly different

It can be assumed from the Duncan MRT in Table 5 that biopellet with 20% bark content is preferred for biopellet production, despite its calorific value is lower than that of biopellet prepared merely of bark (100% bark content). As stated previously, the relatively limited quantity of bark produce by the agathis stands hinders the production of biopellet merely made of the barks. The increase of calorific value by increasing bark content in the biopellet has been well known. Bark contains a higher amount of lignin and extractives compared to that of the wood. Lignin and extractives are carbonous substances with relatively high calorific value. Therefore, calorific value of biopellet is positively correlated to the lignin Klason and extractives content [27].

3.3. Thermal analysis

Thermal analysis was done for wood biopellet (0% bark content/B0), biopellet with 30% bark content (B30) and biopellet of bark (100% bark content/B100). The thermogravimetric of the B0, B30, and B100 is depicted in Figure 2, 3, and 4, respectively. Degradation pattern of biopellet follows the commonly occurred for biomass that consists of three steps [28-30]. Evaporation of water (moisture loss) occurred at the first step, and followed by the decomposition of cellulose, hemicellulose and lignin in the second step. The third step is the residual combustion (burnout residue) characterized by a constant mass loss. Decomposition in the second step consists of decomposition I (volatilization) and decomposition II (burning) [28].
**Figure 2.** Thermogravimetric of the agathis wood biopellet (B0)

**Figure 3.** Thermogravimetric of the biopellet with 30% bark content (B30)

**Figure 4.** Thermogravimetric of the biopellet with 100% bark content (B100)
Table 6. Thermal analysis of biopellet

| Note                           | Sample  |   |   |
|-------------------------------|---------|---|---|
|                               | B0      | B30 | B100 |
| Water loss temperature (°C)   | 36-100  | 36-100 | 37-100 |
| Peak temperature (°C)         | 60      | 64  | 69  |
| Mass loss (%)                 |         |     |     |
| Decomposition I               | 50.01   | 50.58 | 45.90 |
| Decomposition II              | 27.33   | 29.93 | 34.40 |
| Mass loss temperature (°C)    |         |     |     |
| Decomposition I               | 100-350 | 100-352 | 100-359 |
| Decomposition II              | 350-476 | 352-468 | 359-474 |
| Peak temperature (°C)         |         |     |     |
| Decomposition I               | 328     | 329  | 330  |
| Decomposition II              | 467     | 465  | 448  |
| Constant mass loss temperature (°C) | >476 | >468 | >474 |

Thermogravimetric in Figure 2, 3, and 4 and Table 6 indicate that water loss occurred at 36-100°C. That was a little lower than 125°C as reported by several previous works [28-31]. The peak temperature of B100 was higher than these of B0 and B30, which could be brought about by the higher moisture content of biopellet made of 100% bark. Decomposition of biopellet occurred at 100-476°C with total mass loss of 77.34-80.15%. Table 6 shows that mass loss at the first decomposition was of 45.90-50.58% and at the second decomposition the mass loss was of 27.33-34.40%. The mass loss temperature at the first decomposition occurred at 100-359°C, where all of carbohydrate decomposed. Hemicellulose decomposes at the temperature of below 275°C and cellulose at 200-340°C and lignin at 250-360°C [30]. Mass loss of B100 at the first was the lowest due to its lowest carbohydrate content. At the second mass loss that occurred at 350-474°C, lignin is much decomposed. Because of the lignin content of B100 is higher than these of B0 and B30, the highest mass loss was experienced by B100. Mass loss pattern in the present results is similar than that found by Gil et al. [29] for pinewood, eucalypt, chestnut, and cellulose residue which was of 60-70% at the first decomposition and of 25-30% at the second decomposition. Mass loss of biomass generally occurred up to 500°C [31]. In the present results, a constant mass loss occurred at 468-476°C. Considering the temperature of mass loss, pelletizing temperature should be carried out at the temperature of below 200°C in order to increase energy density and avoid significant mass loss.

4. Conclusion
The peeled-off bark of agathis wood can be used to fortify agathis wood biopellet with an acceptable quality and calorific value at 20% bark content. Except for the biopellet density and durability, all biopellet quality parameters satisfied the requirement of DIN EN 14961-2 and 51731 standard. Considering the bark resources and efficiency of pelletizing temperature, the most acceptable biopellet quality could be prepared from particle size of 40-60 mesh with 20% of bark content and pelletizing temperature of 130°C. Based on thermal properties of the bark, wood and biopellet of the agathis wood, pelletizing temperature should be approximatly at 140°C.

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