

# Mini Review Valorization of rambutan (Nephelium lappaceum) by-products: Food and non-food perspectives

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#### Article history

<u>Abstract</u>

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#### **Keywords**

Rambutan By-products Seed oil Nutritional Food applications Tropical fruits are of great significance in human diet due to abundant nutritional and antioxidants components. The processing or consumption of these fruits generates waste, which is generally disposed of into the ecosystem. However, efforts are in line to evaluate the nutritional worth and possible reuse of fruit processing waste by valorizing the waste in an optimal way. In this review, by-products of rambutan fruit waste, i.e., seed and peel, are signified with respect to their nutritional values and possible applications. Peel and seed cumulatively share almost around 50% of whole rambutan fruit by weight. Peel that is rich in phenolics and ellagitannins have applications as a natural antioxidant system. However, abundant fat content (14-41%) with high oleic acid, renders the seed a novel source of vegetable fat. Besides, possibilities of using seed fat in chocolate (30 wt.% substitute) and personal care products are also one of the focus. Nanostructured seed fat is reported for encapsulation off at-soluble vitamins (e.g., vitamin E). Additionally, the seed contains the most of the essential and non-essential amino acids that are concentrated as protein concentrate. The physico-functional properties of defatted seed flour and seed mucilage are also elaborated. Similarly, rambutan seed oil and peel utility as filler in packaging, bio-coagulant, bio-sorbent and alternative biodiesel are also mentioned. Despite diverse applications, gaps are still there to further evaluate and validate the potential of rambutan processing by-products. Thus, to avail the manifold potential, fruit by-products' applications should be scaled up to transform the maximum waste into best.

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# Introduction

Due to miscellany in the ecosystem, Asia is blessed with a rich diversity of over 500 fruit species with almost 70 fruits of major and minor significance that are practically cultivated (Mal et al., 2010). Nonetheless, only 15-20 species, including rambutan are well recognized and cultivated on a commercial scale (Arora, 1994). The most of the tropical fruits are consumed fresh, due to their refreshing taste and nutritional values, while processing results in products such as juices, jam, jellies, pickles and natural flavors (Mal et al., 2010). However, processing industry produces a significant amount of by-products that are generally discarded as waste. Attempts have been made to reduce this environmental waste burden by exploring the nutritional potentials and reuse in food applications (Okolie et al., 2012; Singh et al., 2013). In this continuum, different fruits'peels and seeds are evaluated for possible production of new food sources (unconventional oils) or dietary supplements (antioxidants or protein concentrates). Studies about nutritional valorization of some fruit seeds, such as guava and grape are well documented (Piombo et al., 2006; Yousefi *et al.*, 2013). Rambutan (*Nephelium lappaceum* L.) is one of the potential candidates because almost 50% of the fruit weight is contributed by peel and seed, which is a waste by-product of its processing.

Rambutan is a fruit of Sapindaceae family and is a native to tropical regions of Southeast Asia, such as Indonesia, Malaysia, and Thailand (Tindall, 1994). The name for rambutan fruit is derived from the Malay-Indonesian word "rambut" meaning hairy, thus, sometimes it is also named as "hairy litchi" (Morton, 1987). The fruit is an ovoid berry, yellow to orange-red, or bright-red to maroon in color. It has the leathery skin of ca. 3 mm thickness, fully covered with spinterns of variable length (0.5-2.0 cm). The flesh is juicy and translucent whitish, sweet to very mild sour in flavor. The fruit core has an almond-like seed that is oblong, with dimensions of 2.5-3.4 cm length and 1.0–1.5 cm breadth (Morton, 1987). The rambutan fruit is non-climacteric and is picked up ripe (Figure 1).

In tropical Asia, above 200 clones of rambutan are selected and Malaysia holds the most diverse range of cultivated and wild rambutan species

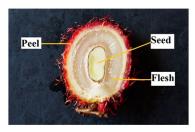


Figure 1. Diagram of rambutan fruit

(Morton, 1987; Tindall, 1994). In terms of rambutan production, Malaysia was ranked as the third (in 2005) after Thailand and Indonesia. The major Malaysian cultivars are Gula Batu, Muar Gading, Khaw Tow Bak, Lee Long, and Daun Hijau (Anonymous, 2015). The fruit pulp, being colorless has no pigments of bioactive nature, but the peel has a diversity of phenolic acids, such as coumaric, caffeic, ellagic, gallic and syringic acid (Thitilertdecha *et al.*, 2010; Sun *et al.*, 2012). Rambutan fragrance is due to the presence of volatiles, namely cinnamic acid,  $\beta$ -damascenone, phenylacetic acid and vanillin (Ong *et al.*, 1998).

A rambutan tree can yield almost 60-70 kg of fruit, and a mature orchard may produce up to 20 tons per hectare (Morton, 1987). Due to shorter shelf life at ambient temperature, rambutan is also consumed fresh and is favored due to the bright color, striking appearance and characteristic flavor (Perera et al., 2012). Nevertheless, processed products from the fruit are also produced and consumed. The fruit weighs 22.4–64.7 g, based on cultivar and agronomic conditions (Augustin and Chua, 1988; Solís-Fuentes et al., 2010; Arenas et al., 2011). Fruit peel contributes almost half to the weight of whole fruit, whereas seed only shares 4.0-9.5 wt.% (Augustin and Chua, 1988; Solís-Fuentes et al., 2010). The waste generated from the processing of fruit could be utilized in various food and non-food applications. Thus, the current review will highlight the nutritional composition and antioxidants of rambutan fruit processing byproducts and further elaborate on the most of food and non-food applications known to date.

#### Rambutan fruit peels

#### Peel chemical composition

Fruit peel or rind is a natural protective covering around the edible flesh that stabilizes fruit integrity. Depending on the cultivar and maturity, rambutan fruit peel adds up to 50% of the total fruit weight (Augustin and Chua, 1988; Solís-Fuentes *et al.*, 2010). The nutritional value of the peel is summarized in Table 1. In addition to nutritional components, some antinutritional compounds are present too, such as saponins, alkaloids, tannins, phytates, and oxalates,

Table 1. Rambutan fruit peel chemical composition

Ingredient	Amount	Reference
Moisture (g 100 g <sup>-1</sup> )	72.05	(Fila <i>et al</i> ., 2013)
Lipids (g 100 g <sup>-1</sup> )	0.23	
Carbohydrates (g 100 g <sup>-1</sup> )	23.78	
Protein (g 100 g <sup>-1</sup> )	2.04	
Fiber (g 100 g <sup>-1</sup> )	0.7	
Ash (g 100 g <sup>-1</sup> )	1.2	
Vitamins		(Johnson <i>et al</i> ., 2013)
carotene (µg 100 g⁻¹)	10.60	
thiamine (mg 100 g <sup>-1</sup> )	0.04	
riboflavin (mg 100 g <sup>-1</sup> )	0.06	
niacin (mg 100 g <sup>-1</sup> )	0.31	
ascorbic acid (mg 100 g <sup>-1</sup> )	7.43	

with respective values of 0.53, 2.17, 1.35, 0.17 and 0.12 g 100 g<sup>-1</sup> (Fila *et al.*, 2012). Nonetheless, these antinutritionals are also credited for diverse bioactivities due to the antioxidant properties. Moreover, similar to citrus peel, rambutan peel also has pectin in the cell wall structure, but the amount is comparatively lower. In fresh rambutan peel, 1.05 to 1.9 wt.% pectin is present. The extracted pectin is dark in color with low methoxy content (11.0– 11.7%) having 43 wt.% moisture and 8.73 wt.% ash. However, the rambutan peel pectin has lower water solubility in comparison to pomelo pectin (Suhaila and Zaharah, 1995; Normah and Hasnah, 2000).

#### Rambutan peel antioxidants

Interestingly, peels of some fruits present greater bioactivity than the edible portion, due to better antioxidants profile (Jayaprakasha et al., 2001). This is true in the case of rambutan fruit as well. Phenolic acids and ellagitannins are the primary antioxidants that contribute to the functionality of rambutan peel (Thitilertdecha et al., 2010; Palanisamy et al., 2011).Palanisamy et al. (2008) evaluated antioxidant activity via the total phenolics of the peel and found the peel as a potent source of natural antioxidants. Free radical scavenging activity of peel ethanol extract was also confirmed by Okonogi et al. (2007). Peel ethanolic extract presented high total phenolics (762 mg GAE g<sup>-1</sup> extract) which were comparable to the commercially prepared grape seed extract (Palanisamy et al., 2008). Gusman and Tsai (2015) evaluated antioxidants for red and yellow rambutan cultivars using conventional extraction (12 h) and ultrasonic extraction (2 min). Enhanced recovery and higher total phenolics with better ferric reducing ability were seen for sonicated extract. Interestingly, 20% increase in the total phenolics and 8% increase in ferric reducing ability (FRAP) were noticed when sonication was used for extraction. Similarly, Thitilertdecha et al. (2010) extracted peel phenolics and tested their lipid peroxidation scavenging activities. In a 100 g of a methanolic extract of peel, coraligin (71.9 mg), ellagic acid (53.5 mg) and geraniin (568.0 mg) were presented. Moreover, in comparison with synthetic antioxidant,

Table 2. Chemical composition of rambutan seed

Component	Amount	Reference
Moisture (g 100 g <sup>-1</sup> )	34.28-34.6	(Fila <i>et al.</i> , 2013; Augustin and
Lipids (g 100 g <sup>-1</sup> )	18.19-38.9	Chua, 1988)
Carbohydrates (g 100 g <sup>-1</sup> )	33.65-61.6	
		(Fila <i>et al.</i> , 2013; Maisuthisakul <i>et</i>
Protein (g 100 g <sup>-1</sup> )	11.06-14.1	al., 2008)
Fiber (g 100 g <sup>-1</sup> )	0.62-6.6	(Fila <i>et al</i> ., 2013; Augustin and
Ash (g 100 g <sup>-1</sup> )		Chua, 1988)
	2.20-2.9	
Minerals (mg 100g <sup>-1</sup> )		(Maisuthisakulet al., 2008)
calcium	30.4	
iron	2.80	
Vitamins		(Johnson <i>et al.</i> , 2013)
carotene (µg 100 g⁻¹)	3.42	
thiamine (mg 100 g <sup>-1</sup> )	0.02	
ribofla∨in (mg 100 g⁻¹)	0.09	
niacin (mg 100 g <sup>-1</sup> )	0.08	

i.e., butylated hydroxytoluene (BHT), the rambutan extract depicted 77-186 fold improved activity against lipid peroxidation. According to Palanisamy et al. (2011), in dried rambutan peel extract, geraniin contributes 37.9 mg g<sup>-1</sup>. Later, corilagin and ellagic acids were confirmed in the peel with respective concentrations of 0.47 and 0.14 mg g<sup>-1</sup> (Samuagam et al., 2014). Muhtadi et al. (2014) evaluated the antioxidant activity of peel using four solvents, namely ethyl acetate, hexane, chloroform, and methanol. The highest bioactivity was presented by ethyl acetate. In comparison with vitamin E, greater bioactivity was observed for extract in terms of IC<sub>50</sub>value (a concentration where the bioactivity reduced to half) that was 7.74 µg mL<sup>-1</sup> for peel and 8.48  $\mu$ g mL<sup>-1</sup> for vitamin E.

Ellagic acid is one of the secondary metabolites in plant cell vacuole. It is well known to possess antioxidant, anti-atherogenic, antiproliferative and chemopreventive properties (Atkinson *et al.*, 2006). Geraniin is a crystalline ellagitannin (Okuda, 2005; Liu *et al.*, 2010) and studies have clarified its antioxidant, nitrous oxide (NO) scavenging and anticancer potentials (Okabe *et al.*, 2001; Wongnoppavich *et al.*, 2009; Thitilertdecha *et al.*, 2010). Purified geraniin has successfully extracted from rambutan peel with avariable yield of 10–20% (Perera *et al.*, 2012; Elendran *et al.*, 2015).

# Rambutan seeds

#### Seed chemical composition

Rambutan seed is considered as a waste product in fruit processing industry. However, roasted seeds are edible and consumed in some Asian countries (Tindall, 1994; Solís-Fuentes *et al.*, 2010). In whole rambutan fruit, the flattened oblong seed shares 4.0-9.5% in the total weight (Augustin and Chua, 1988; Solís-Fuentes *et al.*, 2010; Sirisompong *et al.*, 2011). Table 2 presents the crude chemical composition of rambutan seed. However, dried seed depicted higher proteins, fats and carbohydrate contents (Fila *et al.*, 2013). Amino acid profile of defatted seed flour presents a high-quality protein because of the presence of the most of essential and non-essential ones (Augustin and Chua, 1988). In the case of essential amino acids, their relative amounts are present in seed in the decreasing order from lysine, leucine, valine, isoleucine, phenylalanine, methionine to histidine. However, non-essential amino acids are present in the descending order of relative percentages as: glutamic acid > glycine> aspartic acid > arginine > serine >threonine > alanine > tyrosine > proline > cysteine (Augustin and Chua, 1988). The main fatty acids are palmitic acid (4.36-4.86%), stearic acid (5.93-7.49%), oleic acid (37.91–40.15%) and arachidic acid (36.14–36.77%) (Solís-Fuentes et al., 2010; Sirisompong et al., 2011; Manaf et al., 2013). Table 3 contains the complete profile of seed's saturated and unsaturated fatty acids. In a study by Chimplee and Klinkesorn (2015), the effect of seed moisture content on the extracted fat yield was evaluated. It was suggested that a drying temperature of 65 °C proved best in lowering the seed moisture and improving the extraction yield significantly. Whereas, the seed moisture variation did not make any significant change in fatty acid concentrations. However, in fatty acids, palmitic, palmitoleic, stearic, oleic, linoleic, arachidic, eicosanoic, behenic and erucic acid were found. In agreement with previous studies, oleic (38%) and arachidic acid (36%) were higher in an amount at all the studied moisture levels (4, 11 and 24%) (Chimplee and Klinkesorn, 2015). Besides, fresh seeds contain some antinutritional compounds (mg 100 g<sup>-1</sup>), such as saponins (0.98), alkaloids (0.82), tannins (0.15), phytates (0.40) and oxalates (0.26) (Fila *et al.*, 2012). However, about 50% and 60% reduction in tannins and saponins, respectively, were observed after ten days of fermentation (Olaniyi and Mehdizadeh, 2013). Moreover, recently, atrypsin inhibitor in the fresh seed is also identified by Fang and Ng (2015).

#### Antioxidants in seeds

Various bioactive compounds, such as phenols and carotenoids have been determined in the seed

Composition (%)	а	b	С	d
Saturated				
Myristic acid (C <sub>14:0</sub> )	0.02	0.01	-	0.13
Palmitic acid (C <sub>16:0</sub> )	4.69	7.39	6.1	4.60
Stearic acid (C18:0)	7.03	16.58	7.1	7.88
Arachidic acid (C20:0)	34.32	12.34	34.5	31.53
Heneicosanoic acid (C21:0)	0.05	-	-	-
Behenic acid (C22:0)	3.10	8.91	2.9	2.10
Tricosanoic acid (C23:0)	0.03	-	-	-
Lignoceric acid (C <sub>24:0</sub> )	0.33	-	-	-
Mono-unsaturated				
Palmitoleic acid (C16:1)	0.49	0.49	1.5	0.72
Elaidic acid (C18:1)	0.03	0.02	-	-
Oleic acid (C18:1)	36.79	52.18	40.3	43.09
Gadoleic acid (C20:1)	-	-	-	5.89
Erucic acid (C22:1)	0.66	-	-	0.10
Poly-unsaturated				
Linolenic acid (C18:3)	6.48	2.02	_	0.74
Linoleic acid (C <sub>18:2</sub> )	1.37	-	-	3.22
Eicosadienoic acid (C20:2)	0.04	-	-	-

Table 3. Fatty acid composition of rambutan seed lipids

a) Sirisompong *et al.* (2011); b) Eiamwat *et al.* (2014); c) Solís-Fuentes *et al.* (2010); d) Manaf *et al.* (2013).

using different extraction solvents, i.e., water, butanol, hexane, ethanol, ether, ethyl acetate and methanol (Thitilertdecha et al., 2008; Chunglok et al., 2014; Soeng et al., 2015; Fidriannyet al., 2015). Maisuthisakul et al. (2008) found that the seed ethanolic extract contains total phenols as 43.5 mg g<sup>-1</sup> GAE (gallic acid equivalent) and flavonoids as 13.3 mg g<sup>-1</sup> RE (rutin equivalent). Similarly, dried seed methanolic and ethanolic extracts presented total phenolics as 124.14 and 3.05 mg GAE  $g^{-1}$ , respectively (Chunglok et al., 2014; Fidrianny et al., 2015).  $IC_{50}$  of methanolic and ethanolic extracts were calculated via DPPH and ABTS (Trolox equivalent antioxidant) assays and were found to be 7.0 and 7.34 µg mL<sup>-1</sup>, respectively. Thitilertdecha et al. (2008) also reported antioxidant potentials of different extracts (water, methanol, and ethanol) via reducing power, free radical scavenging, linoleic peroxidation and β-carotene bleaching assays. Likewise, Soeng et al. (2015) determined antioxidant properties of ethanolic extract in terms of superoxide-dismutase assay (SOD). The extract was fractionated into water, butanol, ethyl acetate and hexane. The most active fraction was ethyl acetate followed by water, with the respective concentrations of 3.37 and 3.03  $\mu$ g mL<sup>-1</sup>.

# Rambutan seed lipids

#### Physicochemical properties of lipids

Rambutan seed is reported to contain high amount of lipids (14–41%) (Augustin and Chua, 1988; Solís-Fuentes *et al.*, 2010; Sirisompong *et al.*, 2011; Manaf *et al.*, 2013). Some studies have focused on rambutan seed lipids' physicochemical and thermal properties, and found it interesting for specific applications in the food industry (Solís-Fuentes *et al.*, 2010; Sirisompong *et al.*, 2011). At room temperature, the extracted fat is white in color with lightness  $(L^*)$  86.87, yellowness  $(b^*)$  3.55 and greenness  $(a^*)$  –2.06. In the case of melted fat, these parameters changed to  $L^*$  (66.34),  $b^*$  (6.62) and  $a^*$  (–2.31). However, the refractive index is 1.469, while slip melting point is 38.47°C (Sonwai and Ponprachanuvut, 2012). Similarly, acid value is 0.77 (% oleic acid) and iodine value is 32.31 (g I<sub>2</sub> 100 g<sup>-1</sup> fat). While, saponification value is 199.38 (mg KOH g<sup>-1</sup> fat) with a small fraction of unsaponifiable matter (0.19 g 100 g<sup>-1</sup>). Besides, phytosterols (mg g<sup>-1</sup>), namely  $\beta$ -sitosterol (0.61), stigmasterol (0.32) and  $\alpha$ -tocopherol (0.10) are also present (Sirisompong *et al.*, 2011).

# Fatty acids and triglycerides composition of seed lipids

Lipids functional properties are determined by their structural composition (Reddy and Jeyarani, 2001). Sirisompong et al. (2011) described that seed fat is composed of 49.6 and 45.9 g 100 g<sup>-1</sup> of saturated and unsaturated fatty acids, respectively. The main fatty acids are arachidic acid (C20:0) with 34.3 g 100 g<sup>-1</sup> followed by 36.8 g 100 g<sup>-1</sup> of oleic acid (C18:1). In another study, the main fatty acids determined were the oleic acid (40.45%) and arachidic acid (36.36%) (Harahap et al., 2011). Additionally, palmitic, gondoic, behenic, stearic and palmitoleic acids were also present. Similarly, Sonwai and Ponprachanuvut (2012) also reported that the arachidic acid (C20:0) and oleic acid (C18:1) were the major fractions of seed fats with 42.5% and 33.13%, respectively, whereas stearic acid (C18:0) and palmitic acid (C16:0) contributing 8.70% and 3.38%, respectively. Earlier, Azam et al. (2005) also reported somewhat similar proportions of main fatty

acids. Interestingly, the higher arachidic acid make it suitable for food application without subjecting to further hydrogenation process, especially, when autoxidation is a concern. Chemically, a triglyceride is an ester obtained by the reaction of glycerol (a sugar alcohol) with three fatty acids. Fatty acids could be of same carbon chain length or different and may be saturated or unsaturated. Triglycerides are the major contributor in plant lipids, and rambutan seed fat contains triglycerides in following pattern: 1-arachidoyl-2,3-dioleoylglycerol (AOO) > 1-arachidoyl-2-steareoyl-3-oleoylglycerol (ASO) > 1-arachydoyl-2-oleoyl-3-palmitoglycerol (AOP) > 1-arachidyl-2-stearoyl-3-palmitoylglycerol (ASP) > 1-arachidyl-2-linoleoyl-3-palmitoylglycerol (ALP) > 1-arachidyl-2-linolenyl-oleoylglycerol (ALnO) > 1-arachidyl-2-linolenyl-3-stearoylglycerol (ALnS) > tri-olein (OOO) > tri-archidin (AAA) > 1-arachidyl-2-linoleoyl-3-oleoylglycerol (ALO)(Figure 2). In this sequence, the first three triglycerides, such as AOO, ASO, and AOP make up 77.74% of the total triglycerides. Further, it was revealed that two major types of fatty acids, namely arachidic acid and oleic acid were present in seed triglycerides (Harahap et al., 2011; Sirisompong et al., 2011; Sonwai and Ponprachanuvut, 2012). Manaf et al. (2013) also evaluated the seed triglycerides' composition and confirmed their high molecular weights. By lacking some triglycerides standards, the identification was made based on carbon number using reverse phase high performance liquid chromatography (HPLC). Mainly  $C_{56}$ ,  $C_{58}$ , and  $C_{60}$  were identified, and similar to other studies, arachidic and oleic acids mixtures were proposed to be responsible for long-chain glycerides. Earlier, Kheiri and Mohd. Som (1987) investigated the triglycerides of eight rambutan clones. It was found that C<sub>50</sub>, C<sub>52</sub>, C<sub>54</sub>, C<sub>56</sub>, C<sub>58</sub> and C<sub>60</sub>were present ranging 0-1.2%, 0-7.0%, 12.5-21.6%, 34.6-39.1%, 28.8-47.2% and 1.5-6.6%, respectively.

### Seed solid-fat content (SFC)

Extracted lipids are broadly categorized as oil or fats, depending upon the solid fat content (SFC). In rambutan seed fat, the SFC was studied by differential scanning calorimetry (DSC) (Solís-Fuentes *et al.*, 2010). According to the thermal profile, SFC was 47.8 wt.% at 10 °C that reduced to 25 wt.% by another increment of 10 °C, and complete fusion was observed at 51.8 °C. This higher melting point is related to the presence of long chain saturated fatty acids and high molecular weight triglycerides. Contrary to this report, Sonwai and Ponprachanuvut (2012) found that solid fat was no more present at 40 °C. Similarly, Manaf *et al.* (2013) found 53.5 wt.%

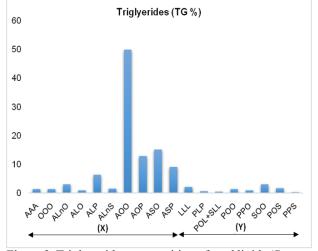


Figure 2. Triglycerides composition of seed lipids (Source: (X) Harahap *et al.*, 2011; (Y) Manaf *et al.*, 2013)

solid fat at 0 °C, whilst at 40°C all the solid fat was fused to oil. Furthermore, it was noticed that between 25-30 °C, the solid fat was just comparable to palm oil, mee fat and lard (Manaf *et al.*, 2012; Manaf *et al.*, 2011). Thus, this behavior might help rambutan seed fat to be stable and resistant to exudation at room temperature, and it could be used for product stability.

#### Fat crystallization behavior

Fat crystal polymorphism indicates the presence of structural similarities among fats of different sources and is an important attribute for its functional characterization (Reddy and Jeyarani, 2001). Seed fat starts to solidify before reaching the temperature of crystallization as observed in the static isothermal mode of capillary X-ray diffractometer (Sonwai and Ponprachanuvut, 2012). The presence of peaks at 3.85°A and 4.24°A justifies  $\beta$  -structure, whereas the peak at 4.15°A relates to pseudo- $\beta$ . Nevertheless, the diffraction peak at 4.55°A is associated to β-structure of fat crystals. After a storage of 7 days, the only dominant peak was observed at 4.60°A, suggesting a typical  $\beta$ -structure. Detailed study of morphology advocated that crystals are loosely-packed spherulites and almost aggregated in a smoother appearance. Sirisompong et al. (2011) also reported that the fat crystals are constituted by  $\beta$  - and  $\beta$ -forms with respective percentages of 15.3% and 84.7%. Like cocoa butter, rambutan seed fat also presents β-form of crystals, signifying its replacement for cocoa butter in processed food products. Recently, Luma and Yang (2016) recounted that rambutan seed fat could be blended with cocoa butter (as filler) up to a certain proportion to get the cocoa butter like functionality.

# Seed lipids thermal stability

Thermal stability is critical for any fat for the

intended use in food processing. Solís-Fuentes et al. (2010) determined the thermal stability of rambutan fat by thermogravimetric analysis (TGA) in an inert  $(N_2)$  and oxidizing environments. The change in mass with temperature was evaluated from 25-1000 °C, with a heating rate of 10 °C/min. Initiation of mass loss and decomposition took place at 240 °C in the N<sub>2</sub> environment. The maximum loss in mass was seen at two temperatures: at 281 °C where the loss rate was 1.84% min/°C, and at 409 °C with a loss rate of 2.11% min/°C. Conclusively, the temperature of final decomposition was 475 °C. On the contrary, in the oxidizing (air) atmosphere, the initial decomposition temperature was lower (237.3 °C) than the inert atmosphere. However, the final decomposition was observed higher at a temperature of 529 °C. A threestage decomposition was noticed in anoxidizing atmosphere with the maxima at 278.8, 399.6 and 512.6 °C. Nonetheless, the maximum rate of change of mass was 1.57% min/°C which was observed at 399.6 °C. The decomposition range of temperature was prolonged for oxygen environment indicating fat reaction with oxygen. It is well understood that the fat oxidation is the principal mean of its quality deterioration. However, in the current case, the prolonged process of mass loss of fatty acids under heat was compensated by absorption and the reaction with atmospheric oxygen.

# Application of peels and seeds of rambutan

### Food applications

Much of the by-products that are produced from fruit processing industry are discarded and these cause environmental issues and increase the net processing cost. However, due to the increasing interest of natural supplements and bioactive compounds, attempts to valorize the by-products are destined to get maximum benefits. Various studies have been conducted to examine the probability of production of antioxidants, prebiotics and other healthy ingredients from fruit waste. In line to this, rambutan waste by-products are getting attention as a raw material or ingredient for multifarious applications in food or non-food commodities. Figure 3 is presenting a summary of all the food applications of rambutan fruit processing by-products.

# Peel extract as antioxidant in oil

Oxidative rancidity of edible oil is one of the major reasons for quality deterioration, where many off-flavor compounds are developed that render the oil unsuitable for consumption. In particular, plant oils are more prone to this quality defect because of

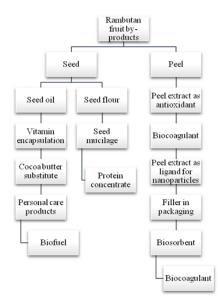


Figure 3. Food and non-food applications of rambutan fruit processing by-products

more unsaturated fatty acids in their structures. Thus, different types of synthetic antioxidants are added in oils to prolong shelf stability and preserve the taste. However, the growing concern of chemicals in food products is disliked and avoided, and natural sources of antioxidants are explored. In a study, peel ethanolic extract was added in sunflower oil in comparison with tocopherols and butylated-hydroxyanisole (BHA). An accelerated storage study (60 °C for 24 days) was conducted and the efficacy of rambutan extract was evaluated regarding free fatty acid generation, iodine value, peroxide value, p-anisidine value and thiobarbituric acid assays. It was observed that extract imparted significantly higher oxidative stability to the oil than control at all the studied concentrations (100, 200 and 300 ppm). In another experiment, oil augmented with different extract fractions (300 ppm) was kept for a 2-year period at room temperature (25 °C). It was observed the extract performed better than tocopherol but found equally effective as BHA (Mei et al., 2014).

# Seed lipids as cocoa butter substitute

Cocoa butter is an integral part of chocolate and confectionary based products. Efforts are made to find a cheaper alternative for this highly demanded ingredient. Rambutan fat as a replacement for cocoa butter is also of great interest for various confectionery products (Issara *et al.*, 2014). Similarly, in another study, Zzaman *et al.* (2014) evaluated the extent of possible replacement of cocoa butter with rambutan seed fat. Interestingly, similar oleic acid contents in rambutan seed fat and cocoa butter were noticed. Rambutan seed fat was blended with cocoa butter at various ratios to estimate how much percentage of cocoa could be replaced without changing the cocoa butter properties. They reported that a blend of 30:70 (rambutan fat to cocoa butter) can provide properties similar to cocoa butter. However, rheologically, at a given shear rate, the rambutan fat presented higher viscosity than the cocoa butter.

In another research, Febrianto et al. (2014) planned a compatibility study between cocoa butter and fermented-roasted rambutan seed fat. Rambutan seed was admixed at 10 to 90 wt.% with cocoa butter by simple melt mixing. The mixtures were studied in two conditions, i.e., unstabilized and stabilized. In stabilization process, the mixtures were stored for 24h at ambient temperature and then conditioned at 5 °C for two weeks. However, in the unstabilized mixture, only melt blending was done followed by solidification. In the case of unstabilized mixing, 30% of the rambutan seed fat imparted somewhat similar properties to that of cocoa butter, but for the stabilized mixtures, 10% and 30% mixture presented a lack of fast fusion and lower solid fat index (SFI) comparing to cocoa butter. It was concluded that at the mixing of 30% or below the seed fat could be used in confectionary products by replacing cocoa butter. In a recent study, Luma and Yang (2016) attempted to mimic cocoa butter properties by blending with rambutan seed fat at 20, 40, 60 and 80%. However, the mixture of 80:20 cocoa butter and rambutan seed fat presented somewhat similar X-ray diffraction peak patterns. In addition, polarized light microscopy data indicated that this mixture has similar crystal morphology to that of cocoa butter. Thus, a careful blending of rambutan fat and cocoa butter may help food processors to mimic cocoa butter properties and replace this high-cost ingredient of chocolate to provide a product of economically cheaper but of similar texture.

# Seed lipids as vitamin carrier

Being an excellent tool for delivery of friable nutrients, micro- and nano-encapsulation techniques are getting more attention nowadays. Additionally, the oriented delivery and slower release of active ingredient are more precise and efficient. Recently, nanostructured-lipid carriers for vitamin E (a fat-soluble vitamin) were prepared by Uraiwan and Satirapipathkul (2016) using melt-emulsification process. The rambutan seed oil and stearic acid (C18:0) were used as liquid and solid lipids respectively, and Tween-20 was used as a surfactant, and vitamin E was entrapped. At higher surfactant concentration, smaller nanoparticles of better stability were obtained; however, an optimum surfactant concentration was found as 5 wt.% with

nanoparticles of 139.43 nm size. It was claimed that rambutan seed oil could be a potential carrier for fat soluble vitamins and other bioactive compounds of this nature.

# Seed flour as stabilizer and thickener

Post extraction of fat from rambutan seed the obtained defatted seed flour could be considered a promising source of carbohydrates (87.04%) and proteins (10.07%)(Eiamwat et al., 2015). A higher percentage of amylose (32.16%) is also reported in the defatted seed. The defatted flour presented good viscometric properties with a maximum viscosity of 1300 cP (centipoise). It was proposed that the flour could be used in confectionery products as a thickener. In a recent study, it was observed that defatted flour, after dilute alkali (0.075N NaOH) treatment, presented lower solubility, turbidity, and oil absorption. On the contrary, improved bulk density, water absorption, swelling power, emulsion capacity, and stability were noticed after alkali treatment. The least gelation concentration (the least amount to make gel) was also decreased, indicating it to be an excellent thickener, and a non-conventional source of protein and starch (Eiamwat et al., 2016). Earlier, rambutan seed flour (2%) has been tested as a low-calorie thickener for replacement of egg yolk or vegetable oil in the formulation of 'Thousand Island Dressing' (Phanthanapratet et al., 2012). The prepared dressing indicated a fourfold lowering in calorific value than the regular recipe. Moreover, 63% of the panelists were satisfied with the sensory attributes of the dressings.

#### Seed protein concentrate

Protein concentrates are human dietary supplements that are rich in proteins. A variety of protein concentrates of animal and plant origin are available in the market. However, still a continuous search for some cheaper alternatives is in practice. Likewise, rambutan seed has a high amount of protein ranging 10.07 to 16.21%; has been proposed as a non-conventional protein source (Augustin and Chua, 1988; Maisuthisakul et al., 2008; Fila et al., 2013; Eiamwat et al., 2015). Moreover, the presence of majority of essential and non-essential amino acids advocates its optimum quality (Augustin and Chua, 1988).

Albumins are water-soluble globular proteins that are denatured by heat. They perform a variety of functions in human, such as regulating blood colloidal osmotic balance. The most common source of albumins is egg white. However, recently, Vuong *et al.*(2016) attempted to develop seed-albumin concentrate (80.8%) from rambutan seed. Further characterization presented its maximum solubility at a pH of 4. However, at this pH, oil and water absorption capacities were seen with respective amounts of 6.13 and 0.79 mL g<sup>-1</sup>. The maximum emulsification and foaming capacities were obtained at a pH~12.

# Rambutan seed mucilage

Plant gums and mucilages are very common ingredients in numerous food and non-food formulations. Gums are higher molecular weight substances and usually used as an additive in low concentration, usually below 1% in most food products. They act as texture modifier, thickener, stabilizer, emulsifier and fat replacer. In a recent study, rambutan seed mucilage (yield 3.3%) was isolated using water, and ethanol precipitation (Sekar et al., 2015). The extracted water-soluble gum was whitish-brown in color with a lustrous appearance. In water, it gave a neutral and colloidal solution with a swelling index of 9.1. The dried powder indicated a passable flow with the angle of repose of 29.35°. Regarding particle density, tapped and bulk density values were 2.26 and 1.29 g mL<sup>-1</sup>, respectively. Considering its functionality, it could be a potential candidate for various food and pharma applications, either as a food additive or a tablet binding agent.

#### Non-food applications

Where fruits and their waste by-products are presented as novel sources of bioactive ingredients, such as antioxidants and fiber, the trend is there to develop novel materials for non-food applications by using this cheaper raw material. The wise use of fruit waste might help to lower the concerns related to waste management. Moreover, these wastederived components might reduce the alarming risks related to synthetic chemical pollutants. Figure 3 is presenting a summary of all the non-food applications of rambutan fruit processing by-products.

### Seed lipids in personal care products

Natural products with the least side-effects are quite common in cosmetics and personal care products. Similarly, in an attempt Lourith *et al.* (2016) developed liquid soaps and solid bars comprising rambutan seed fat. The authors reported that the fat production method was also estimated for possible scaling up for industrial needs. Furthermore, it was compared with some commercial common sources of vegetable oils. The fat presented a better compatibility with other ingredients of the formulation. Thus, it was proposed that this unconventional fat, like other vegetable oils, could be a potential raw material for

the personal care products.

# Peel extract as ligand in nanoparticles preparation

Nanoparticles from metals are of great interest as they are multifunctional and widely used in pharmacy and personal care products. However, for the production of nanoparticles, a variety of chemical compounds are employed that itself can harm the environment. To reduce the use of chemical agents, green methods are developed and evaluated for suitability. In a study, Yuvakkumar et al. (2014) presented a novel mechanism for the green synthesis of zinc oxide nanocrystals employing rambutan peel extract as a natural ligand. However, a successful synthesis was carried out through zinc-ellagate complexation reaction. Cotton fabric was used to coat these nanocrystals, and their antibacterial activity was assessed through agar disk diffusion. Interestingly, good antibacterial activity was presented by Zn-nanocrystals against Escherichia coli and Staphylococcus aureus. The authors elaborated that this unique green synthesis could be applied effectively in biomedical nanotechnology. In another study, rambutan peel was utilized for zinc oxide nanochains formation, and the success of the experiment was assessed by scanning electron microscopy (SEM). The prepared Zn-nanochains were assessed for anticancer activity against human liver cancer cells (HepG2). The decreased cell viability (40-60%) and altered cell morphology (10-50%) were observed at different days of incubation. Hence, it was suggested that the prepared nanochains have potential anticancer activity (Yuvakkumar et al., 2015).

#### *Peel flour as filler in packaging*

Petroleum based commercial plastics are widely used for developing sheets and films. Among these, polyethylene is one of the major contributors, and the annually huge amount of shopping bags and bottles are produced. The addition of any filler can affect the mechanical properties of the polyethylene. A filler is a substance that is blended with a parent compound either to reduce the production cost or to impart a particular functionality. In an attempt, melt-blending of rambutan peel flour with lowdensity polyethylene (LDPE) was done, and tensile properties were estimated. A maximum of 15% peel flour was mixed, and the results indicated that the addition of rambutan peel flour decreased the tensile strength of polyethylene. However, with increasing flour content and particle size (63-250 µm), higher Young's modulus was observed as compared to neat polyethylene films (Nadhirah et al., 2014).

In another study, the effect of adipic acid addition was evaluated in polyethylene/rambutan peel flour (0-25%) blends. This adipic acid addition resulted in polyethylene films with higher mechanical strength. The higher amount of rambutan flour improved the Young's modulus, but adipic acid reversed the effect (Nadhirah et al., 2015). Earlier, Ooi et al. (2012) evaluated the effect of glycerol or sorbitol (plasticizers) addition in blends of polyvinyl alcohol (PVA) and rambutan peel flour. The addition of glycerol resulted in higher elongation-at-break compared to sorbitol. Conversely, films presented higher Young's modulus and tensile strength when sorbitol was added. For both plasticizers, the water vapor transmission rates of the films were increased; albeit, the sorbitol presented comparatively lower transmission. In biodegradability test, more weight was lost by glycerol or sorbitol plasticized films compared to films without any plasticizer.

# Seed as bio-sorbent

To lower the environmental burden of heavy metals many bio-based sorbents are developed where they are used in filtration process. Njoku et al. (2014) attempted chemical activation of rambutan peel using potassium hydroxide (KOH). However, when microwave heating was employed in conjunction with KOH, activation time was reduced. A typical dye, acid yellow 17, was used as a test adsorbate. Parameters like contact time, pH and dye concentration were manipulated to follow up the process efficiency. At equilibrium time of 4 h, higher adsorption was noticed even for the higher initial concentration of dye. Kinetic studies using the Langmuir model indicated that the dye adsorption was taken place by forming a monolayer with the maximum adsorption capacity of 215.05 mg g<sup>-1</sup>.

# Seed oil as biodiesel

Plant oil and their derivatives have been considered for fuel in diesel engines (Harrington, 1986; Klopfenstein, 1988). However, the availability, cost and technical issues, such as lower stability and higher viscosity should be kept in consideration. The viscosity could be manipulated by replacing glycerol moiety with some simple monohydric alcohols. Nonetheless, the oils with higher iodine values get easily oxidized and lose their efficiency. Kalayasiri *et al.* (1996) found that rambutan seed has a high cetane index of 67.1. A cetane number is parametric to the speed of combustion of diesel fuel and the compression required for its ignition. The presence of a large number of  $C_{20}$  chain lengths in rambutan oil made the cetane index higher. Extracted oils and their

esters indicated a heat of combustion in the range of 40.0–40.4 J/g. So, attempts are made to develop new sources by utilizing rambutan processing by-products as an alternative biofuel.

# Seed as bio-sorbent

With the increasing environmental pollution, there is a serious concern to reduce the pollutants that are dangerously affecting the ecosystem. Different techniques and methods are being tried to minimize environmental pollutants. The waste of fruit and vegetables is transformed into raw or activated powders or manufactured into membranes to remove pollutants by adsorption or filtration. 'Activation' is an approach where heat or chemicals are used for developing natural carbon particles of high surface area. In developed countries, the activated carbon has been used for food and beverages industries in cleaning effluent waste water. Some of the agricultural waste by-products that already reported for developing activated carbon are almond shell (Nabais et al., 2010), avocado kernels (Elizalde-Gonzalez et al., 2007), bamboo waste (Wang et al., 2010) and plum stones (Nowicki et al., 2010). Similarly, Ibrahim et al. (2013) reported rambutan activated carbon as a potential sorbent. A nitrogen environment with two temperatures (450 and 650 °C)was used for developing porous carbon particles. Better surface area and improved total pore volume were noticed in the case of higher temperature, but the yield was reduced for the same.

#### Seed as bio-coagulant

Coagulation is a process of electrostatic charge destabilization and restabilization of particles through opposite charge to make flocs after neutralization. Alum is still widely used in water treatment to remove turbidity through coagulation process due to the wide availability and cost. Abidin et al. (2014) reported rambutan seed efficacy for removal of water turbidity through coagulation method. The study design was optimized in terms of extraction solvent and coagulant concentration (rambutan seed) and pH, and commercial kaolin was the model material to be removed. Results suggested that the best extraction solvent was 1.0 N sodium chloride (NaCl) where almost 99% turbidity was removed. The best working dose of seed was 100g L<sup>-1</sup> at pH of 3. A ratio of 1:1 of alum and seed was also tested and found much better than the alum and seed alone. However, in the case of rambutan seed, bigger flocs with smaller sludge volume were noticed, suggesting it to be a potent biocoagulent in turbidity removal.

# Conclusion

Due to the presence of nutritionally essential elements and bioactive compounds in fruit processing waste, the efforts are directed to valorize this waste. In this respect, by-products of variety tropical fruits have been evaluated including guava, grapes, and rambutan, etc. Rambutan fruit by-products presented an excellent source of phenolic antioxidants and ellagitannins, with immense bioactive potential. Due to the richness of antioxidants, peel extract has successfully been utilized to preserve commercial sunflower oil against oxidation. Rambutan seed, being rich in lipids, is suggested as a novel source of oil. Moreover, physicochemical characterization of seed fat elaborated the thermal stability and abundance of oleic and arachidic acids. Most importantly, up to a certain limit, seed lipids could be replaced with cocoa butter in chocolate and confectionary products. Besides, seed defatted flour, protein concentrate, and mucilage have been proposed for various food applications. Non-food applications of rambutan waste by-products includes personal care products, biomedical, packaging, biodiesel, bio-sorbent, and bio-coagulant. This multifaceted usage of rambutan by-products will help to lessen the mighty tonnage of fruit processing waste by-products. Unfortunately, despite this extensive research on the valorization of rambutan waste, Malaysia has insufficient industrial setup for rambutan processing. Nevertheless, areas are still there to explore, and scaling up is direly needed to get maximum advantage from this locally produced abundant fruit.

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# **Conflict of interest**

Authors have no conflict of interest.

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