The difference between gelatinization, endothermic and pasting properties of sago starch and those of other starches

Ansharullah Ansharullah*[1], Sri Wahyuni[2], and Muhammad Natsir[3]

* Corresponding author: aansharullah@gmail.com
Department of Food Science and Technology, Universitas Halu Oleo, Indonesia

DOI: 10.29322/IJSRP.10.09.2020.p10529
http://dx.doi.org/10.29322/IJSRP.10.09.2020.p10529

Abstract- Properties of gelatinization, endothermic and pasting behaviour of *Metroxylon sp*. sago starch were studied. Those properties of other starches (*Arenga pinnata*, wheat, corn, and cassava) were also analyzed as a comparison. It was found that *Metroxylon* sago starch had a relatively higher gelatinization temperature and endothermic energy, as well as higher peak viscosity. Many potential applications of these starches in the food industry might be made by knowing these properties, in which the search of underutilized starch sources was being pursued.

Index Terms- Arenga, endothermic energy, gelatinization characteristics, pasting, sago.

I. INTRODUCTION

Like other starches, sago starch has been utilized in many application of food products, either as a main raw material or as an additive, such as food, medicine, paper, plywood, and textile industries. Specifically in the area of food industries, starch has been used as texture shapers, gelling agent, bulking agent, anti sticky agent, edible packaging, and fermentation energy [1], [2], [3], [4]. The use of starch in the food application would be dependent upon several factors, such as obtainability, price, easiness of processing, and the quality impact on the applied final product.

Sago is a commodity that produces large quantities of starches that grows in a stable and sustainable ecosystem dynamic. The plant might grow with variations in climate and acid soil conditions. Sago occupies a very strategic position in Indonesia's food history, especially for residents of coastal or lowland areas [5].

This commodity has a great potential to become a staple food and raw material for starch-based industries because it is well known and well-developed in society. The enormous potential of sago should be utilized for the purpose of finding an under-utilized food starch source. A systematic and sustainable development of sago may be a way to secure food sources in the future [6].

There are two major sago starches, i.e. *Metroxylon sp*. and *Arenga sp*, which have many differences in their properties. The former may produce a lot of starch, up to about 250 kg per palm, while the latter only produce about 75 kg per palm [7], [8], [9], [10].

Starch properties, such as gelatinization temperature, endothermic energy, and pasting behavior are very essential to be identified before using them in any food formulation. Therefore, the aims of this research was to portray those properties of sago starch. Its properties were then compared to the properties of arenga, wheat, corn and cassava starches.

II. MATERIALS AND METHOD

1) Materials.
The sample of fresh sago starches (*Metroxylon sp*.) was directly obtained from a small sago processing unit in the Village of Lamokula, Regency of South Konawe, in the Province of Southeast Sulawesi, Indonesia. Meanwhile, the other starches (arenga from *Arenga sp*., wheat, corn, and tapioca) were purchased from a local supermarket.

2) Gelatinization and Endothermic Properties Measurement.
An apparatus of DSC-7 Perkin Elmer, which was calibrated with indium (ΔH 28.45 J/g, melting point 156.6ºC), was used to determine the temperature of thermal transition and endothermic energy (ΔH). Approximately 1 g of sample was energetically mixed with deionized distilled water in a glass capped bottle. The ratio of starch/water was 1:2 (dry basis). About 10-15 mg of this mixture was then balanced directly into a 40μL DSC pan using a micropipette, then sealed immediately. The wrapped pans were kept to stand for 2 h at 24ºC before heating from 20 to 120ºC, at a scanning rate of 10ºC per min. A blank pan was used as reference. Temperatures of thermal transition of the starch were defined in terms of T_o (onset), T_p (peak), and T_e (end) of temperature of gelatinization. Endothermic energy (ΔH) in J/g was determined by integrating the top area of the DSC endothermic graph.

3) Pasting Properties
An apparatus of Rapid Visco Analyzer (RVA) was used to profile the pasting characteristics of the samples. About 2 g of samples (with 14% moisture basis) were balanced directly into the aluminum canister. Then, exactly 25 mL of deionized distilled water was added.

The test in RVA was performed with a 13 min cycle. Initial test was to calibrate for 1 min at 50ºC, followed by heating for 3.75 min to a maximum temperature of 95ºC. The sample was hold for 2.5 min at 95ºC; cooled for 3.75 min until the temperature reached 50ºC; and subsequently hold for 2 min at 50ºC [11], [12]. The profile of the pasting characteristics were peak viscosity, temperature and time at which the peak occurred, minimum viscosity, final viscosity, pasting temperature, breakdown rate (the decrease in viscosity between peak and minimum per min), retrogradation rate (the increase in viscosity per min during cooking from 95 to 50ºC), and the rate of increase in viscosity during 5ºC holding stage. The viscosity was expressed in Rapid Visco Unit (RVU), where one scale of RVU was equivalent to about 12 cPoise.

4) Statistical Analysis
At least three replicates were measured for each sample, and the result average was made. ANOVA (Analysis of variance) was performed using the Minitab® 18.1 statistical package to calculate any statistical differences [13]. To compare among average, a Duncan multiple range test was performed.

III. RESULTS AND DISCUSSION

A. *Properties of Thermal Transition and Energy of Endothermic*

T_o (onset temperature), T_p (peak temperature), T_e (end temperature), and ΔH (endothermic energy) of the samples are shown in Table 1. Sago, arenga, wheat, corn and tapioca samples had a single endotherm of gelatinization.

TABLE 1
PROPERTIES OF THERMAL TRANSITION AND ENDOTHERMIC ENERGY OF SAGO, ARENGA, WHEAT, CORN AND TAPIOCA STARCHES[1,2]

Samples	T_o(ºC)[3]	T_P(ºC)[3]	Te(ºC)[3]	$T_e - T_o$ (ºC)[4]	ΔH (J/g)[5]
Sago	68.20[a]	72.39[a]	80.74[a]	12.54[a]	16.01[a]
Arenga	64.43[b]	68.95[c]	76.93[b]	12.50[a]	12.93[b]
Wheat	53.35[c]	61.06[d]	69.87[c]	14.52[b]	7.76[d]
Corn	65.67[b]	70.05[bc]	76.09[b]	10.42[c]	10.91[c]
Tapioca	62.79[d]	69.08[c]	78.49[d]	15.70[d]	11.76[bc]

[1]The average of triplicates.
[2]The same superscript were not significantly different ($p<0.01$).
[3]T_o, T_p and T_e in ºC were the onset, peak, and end of gelatinization temperature.
[4]Range of gelatinization temperature.
[5]Endothermic energy.

The results obtained indicated that the ranges of gelatinization temperature ($T_e - T_o$) fluctuated between 10.4ºC and 15.7ºC. The temperature ranges of gelatinization for corn starches was not significantly lesser than those reported by the other study [14]. This discrepancy was most likely caused by the difference in rate of heating used during the DSC run, where the present study using a heating rate of 10ºC per min while the latter authors used 16ºC per min. In a separate study, it was revealed that a higher heating rate in DSC test has given an increase in the ranges of gelatinization temperature [15].
The gelatinization temperature range reflected the quality and homogeneity of the crystalline portion of the starch, which includes uniformity of crystal size and stability [16]. The decrease in temperature ranges indicated that the crystal portion formed is more homogeneous so that it required lower energy or enthalpy to melt.
Enthalpy energy (ΔH) of the starch samples fluctuated between 7.76 and 16.01 J/g. The ΔH for corn starch was higher than that found by Khomsatin et.al. [14] and Waterschoot et al. [17]. The value for wheat and cassava starch was slightly similar to that reported by Waterschoot et al.[17].
Gelatinization enthalpy (ΔH) was the heat energy required to release the amylose double helix bonds and destroyed the crystalline part during the gelatinization process. A higher ΔH in sago starch indicated a stronger crystalline amylopectin, making it more difficult to degrade during heating process.

B. *Profile of RVA Pasting Properties*

Profile of RVA pasting properties of the samples are indicated in Figure 1, meanwhile the summary of the pasting properties is shown in Table 2. It was indicated in Figure 1 that there were several differences of the pasting properties of the samples analyzed.

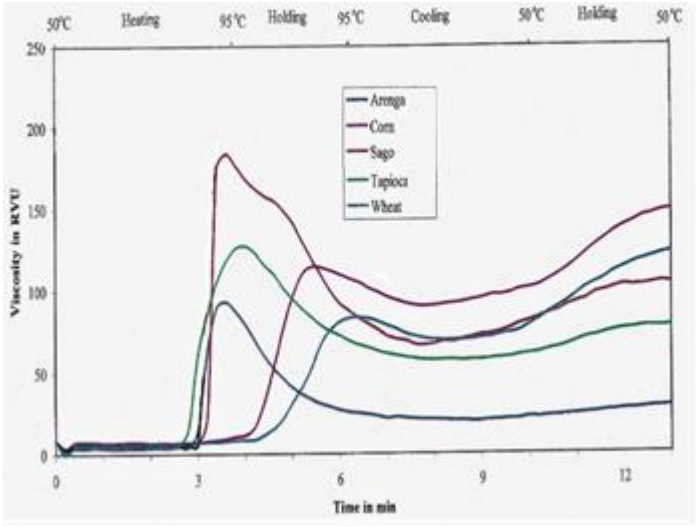

Figure 1. Profile of RVA pasting properties sago, arenga, corn, wheat and tapioca starches.

Figure 1 shows the starch gelatinization profile measured using RVA. The data obtained were peak viscosity, pasting temperature, hot paste viscosity, retrogradation rate, and final viscosity after maintained at 50ºC or cold paste viscosity. The results indicated that peak viscosities of the sago starch were significantly higher than those of other starches. This might be caused by the differences in size of granules, where sago starch has the biggest size among the samples [18]. The peak viscosity was achieved at the end of the heating stage when the quantity of

swollen starch particles increased resulting in pasting state [18]. Pasting occurred when there was a combined effect of swelling and rate of disruption of the granules [19]. There was also an indication that peak viscosity was influenced by the water-holding capacity of the starch [20].

As with native starch, sago starch has a gelatinization profile with a high peak viscosity followed by a sharp breakdown viscosity during the heating phase. This showed that the sago starch granules were less resistant or less stable by the heating process. In the cooling phase, the viscosity of the starch paste increased again due to the re-association of amylose and amylopectin molecules through hydrogen bonds. The increase in viscosity during the cooling phase also shows a trend toward retrogradation of the sago starch paste. The high amylose content has a major contribution to the tendency for starch paste retrogradation during the cooling phase [21], [22], [23].

.

TABLE 2
PROFILES OF RVA PASTING PROPERTIES OF SAGO, ARENGA, WHEAT, CORN AND TAPIOCA STARCHES

RVA pasting properties [1,2]	Starch of				
	Sago	Arenga	Wheat	Corn	Tapioca
Peak viscosity (RVU)	185.91a	94.16c	84.73c	117.68d	128.96e
Peak occured at: Temperature (°C)	81.15a	80.78a	95.00c	95.00c	84.98b
Time (min)	3.50a	3.47a	6.34c	5.48d	3.90b
Minimum viscosity (RVU)	65.72a	20.50c	70.42d	89.62c	57.79f
Final viscosity (RVU)	105.79a	28.13c	121.38 d	149.92c	76.67f
Pasting temperature (°C)	75.10a	72.95c	93.10c	87.93d	70.98e
Breakdown rate (RVU/min)	26.72a	12.87c	7.93d	10.45cd	18.10e
Retrogradation rate (RVU/min)	5.97a	0.64c	5.96a	6.83a	2.34d
Rate of viscosity increasing before peak (RVU/min)	422.12a	139.66c	40.01d	78.10e	97.48f
Rate of viscosity decrease during 95°C holding time (RVU/min)[3]	32.01a	10.83cd	9.27d3	12.13c3	17.19e
Rate of viscosity increase during 50°C holding time (RVU/min)	5.84a	2.32c	12.80d	15.31e	4.36f

[1]Means of duplicates

[2]Mean in row having the same superscript were not significantly different ($p<0.01$)

[3]The values were calculated only from the descending slope starting from the peak because the peak was reached after 95°C.

In many industrial application, a high-viscous type of starch must be initially modified to be used in various food formulation. The knowledge of pasting profiles of the starch might help one to choose the appropriate characteristics.

Cold viscosity of the starch showed ability of samples to make a viscous paste or gel after cooking and cooling. As shown in Table 1, sago starch had the most glutinous paste; while arenga samples exhibited the most aqueous paste.

The starting point of granules breakdown was measured from the temperature and time, where the peak started to occur. The present study revealed that sago and tapioca starches have a more vulnerable granules compared to those of wheat and corn starches. This has given rise to a lower peak temperature of sago starch. Peak temperature of wheat and corn starches were similar at 95°C, but the time of peak of corn starch to occur at 5.48 min, earlier than that of wheat starch at 6.34 min. This was probably related to the lipid content of the samples, where wheat contained more lipid than corn. The assumption was that there was a complex between amylose and lipid, in which it would reduce the water binding capacity, the swelling, solubilization of the wheat starch, resulted in a delay of peak time [18].

The increase of viscosity rate of the RVA curves reflected the homogeneity of the granules. The results of this study indicated that wheat and corn starches had less rates in viscosity increase. Their granules might have swollen over a wider range of temperatures, reflecting that a less homogenous distribution of granules. Meanwhile, sago starch which had a higher viscosity rate indicated a less heterogeneous distribution of granules.

The fragility of the granules to swell during shearing and mixing process might be measured in its breakdown rate. The breakdown was difference between the peak and the lowest viscosity reached during the holding stage. The increase and decrease rate of the paste viscosity would rely on the type and amount of starch, temperature gradient, shear force and composition of the mixture [24], [25].

When the temperature was held constant at 95°C for about 2.5 min, the starches showed a high peak, followed by a high swelling power. This had resulted in an easier rupture of the granules and gave a rapid decrease in viscosity [18]. As shown in Table 1, a higher breakdown rate of sago starch indicated a less stable paste, compared to that of wheat and corn starches. Therefore, a chemical modification, such as cross linking, may be needed if sago starch was to be applied into food formulation that require a hot stable paste, such as sterilization or canning. The resistance of starch to mechanical breakdown may be improved through cross-linking modification

A continues temperature increase after the peak would further disintegrate the swollen granules. This would contain exuded amylose, granules fragments, colloid and molecularly dispersed starch molecules [26].

Last phase of the curve, as the cooling stage, was when the granules were cooled and retrogradation took place. As shown in Figure 1, retrogradation occurred after cooling from 95 to 50°C. During retrogradation, there was an increase in viscosity, which was most likely due to the amalgamation of the fragmented and dispersed granules molecules. Sago starch gave a higher rate, compared to other starches. When the temperature was held constant at 50°C for another 2 min, there was an increase of viscosity of all starch samples. This might be due to the formation of a cohesive network during retrogradation stage.

A review by Balet et al [18] revealed that measuring the pasting characteristics of starch with RVA has several advantages over the amylograph, i.e. easiness and versatility to operate, small

sample size (4 g compared to 65 g); flexibility in setting the temperature profile; and the ability to directly record data in a computer system.

IV. CONCLUSION

Gelatinization temperature, endothermic energy, and profile of RVA pasting properties of several starch samples showed that sago starch sample exhibited a less gelatinization temperature range, compared to that of wheat and tapioca, but it was higher than that of corn. Sago starch had the highest endothermic energy of gelatinization. From the RVA pasting profile, sago starch had the highest peak viscosity amongst the starches studied.

Several pasting characteristics of the sago starch may be useful for certain application in food formulation. In this regard, such properties as higher viscosity may be appropriate for thickener and fruit pie filling. On the other hand, vulnerability of sago starch granules during shearing and mixing at hot temperature may need to be modified, if this starch was to be applied in the products such as canned and sterilized foods. Obviously, a more detailed study is needed to confirm the appropriateness of this starch for the future application.

ACKNOWLEDGMENT

We acknowledge for financial support to Department of Food Science & Technology, Universitas Halu Oleo in carrying out the work.

REFERENCES

[1] S.C. Alcazar-Alay, and M.A.A. Meireles, Physicochemical properties, modifications and applications of starches from different botanical sources. Food Sci.Technol. 2015; DOI: http://dx.doi.org/10.1590/1678-457X.6749.

[2] K. Hirao, T. Kondo, K. Kainuma, and S. Takahashi. “Starch properties and uses as Food for human health and welfare”, Sago Palm - Multiple Contributions to Food Security, and Sustainable Livelihoods, H. Ehara¬• Y.¬Toyoda, and D.V. Johnson, eds, Springer Open. 2018. https://doi.org/10.1007/978-981-10-5269-9.

[3] H. Zhang, Y. Jiang, J. Pan, Y. Lv, J. Liu, S. Zhang, and Y. Zhu. Effect of tea products on the in vitro enzymatic digestibility of starch. Food Chem. Vol. 243, pp. 345–350. 2018.

[4] R.K. Dhall, Advances in Edible Coatings for Fresh Fruits and Vegetables: A Review. Critical Reviews in Food Science and Nutrition. 2013. http://dx.doi.org/10.1080/10408398.2010.541568.

[5] T. Bantacut. Kebijakan pendorong agroindustri tepung dalam prespektif ketahanan pangan. Jurnal PANGAN Vol. 18. No. 53. 2009.

[6] P. Tirta, N. Indrianti, and R. Ekafitri. Potensi tanaman sagu {Metroxylon sp.) dalam mendukung ketahanan pangan di Indonesia. Jurnal PANGAN Vol. 22. No. 1. 2013.

[7] A.A. Karim, A. Pei-Lang Tie, D.M.A. Manan, and I.S.M. Zaidul. Starch from the sago (Metroxylon sagu) palm tree - properties, prospects, and challenges as a new industrial source for food and other uses. Compr. Rev. Food Sci. Safety, Vol. 7, pp. 215-228. 2008.

[8] H. Konuma. “Status and outlook of global food security and the role of underutilized food resources”, Sago Palm - Multiple Contributions to Food Security, and Sustainable Livelihoods, H. Ehara¬• Y.¬Toyoda, and D.V. Johnson, eds, Springer Open. 2018. https://doi.org/10.1007/978-981-10-5269-9.

[9] F.S. Jong. An overview of sago industry development, 1980s–2015, Sago Palm - Multiple Contributions to Food Security, and Sustainable Livelihoods, H. Ehara¬• Y.-Toyoda, and D.V. Johnson, eds, Springer Open. 2018. https://doi.org/10.1007/978-981-10-5269-9.

[10] M. Flach, Sago Palm, Metroxylon sagu Rottb. pp. 33-47. International Plant Genetic Resources Institute. 1997

[11] S-H. Yun and K. Quail. RVA Pasting properties of Australian wheat starches. Starch/Stärke vol. 51, No. 8-9, pp. 274–280. 1999.

[12] D.C. Coronell-Tovar, R.N. Chavez-Jauregui, Á. Bosques-Vega, and M.L. Lopez-Moreno. Characterization of cocoyam (Xanthosoma spp.) corm flour from the Nazareno cultivar 2018. DOI: https://doi.org/10.1590/fst.30017.

[13] C,F. Lee, J. Lee, J-R. Chang, and T. Tai. Essentials of Excel, Excel VBA, SAS and Minitab for Statistical and Financial Analyses. Springer. 2016. DOI: 10.1007/978-3-319-38867-0.

[14] S. Khomsatin, Sugiyono, and B. Haryanto. Study of the effect of steam pressure treatment on the physicochemical properties of corn flour. J. Teknol dan Industri Pangan Vol. 23, no. 1. 2012.

[15] M. Wootton, and A. Bamunuarachchi. . Application of differential scanning calorimetry to starch gelatinization. II. Effect of heating rate and moisture level. Starch/Starke vol. 31, pp. 262-264. 1979.

[16] A. Gunaratne and R. Hoover. Effect of heat-moisture treatment on the structure and physicochemical properties of tuber and root starch. Carbohydrate Polym Vol 49: pp: 425-437. 2002.

[17] J. Waterschoot, S.V. Gomand, E. Fierens and J. A. Delcour. Review: production, structure, physicochemical and functional properties of maize, cassava, wheat, potato and rice starches. Starch/Stärke, vol. 66, pp. 1–16. 2014. DOI 10.1002/star.201300238.

[18] S. Balet, A. Guelpa, G. Fox, and M. Manley. Rapid Visco Analyser (RVA) as a tool for measuring starch-related physiochemical properties in cereals: a review. Food Anal. Methods. July. 2019. https://doi.org/10.1007/s12161-019-01581-w

[19] I.L. Batey. Interpretation of RVA curves. In: Crosbie GB, Ross AS(eds) The RVA Handbook. AACC International, St. Paul, pp 19–31. 2007.

[20] D. Cozzolino, K. Allder, S. Roumeliotis, and J. Eglinton. Feasibility study on the use of multivariate data methods and derivatives to enhance information from barley flour and malt samples analyzed using the Rapid Visco Analyzer. J Cereal Sci vol. 56 pp: 610–614. 2012.

[21] M. Gudmundsson. (1994). Retrogradation of starch and the role of its components. Thermochimica Acta 246: 329- 341. 1994.

[22] U. Lehmann, C. Rossler, D. Schmiedl, and G. Jacobash. Production and physico-chemical characterization of resistant starch type 3 derived from pea. Starch/Nahrung/Food 43: 60-63. 2003.

[23] X. Shu, L. Jia, J. Gao, Y. Sing, H. Zhao, Y. Nakamura, and D. Wu. The influence of chain length of amilopectin on resistant starch in rice (Oryza sativa L). Starch/Starke 59: 504-509. 2007.

[24] Copeland L, Blazek J, Salman H, Tang MC (2009) Form and functionality of starch. Food Hydrocoll 23(6):1527–1534

[25] Schirmer M, Höchstötter A, Jekle M, Arendt E, Becker T (2013) Physicochemical andmorphological characterization of different starches with variable amylose/amylopectin ratio. Food Hydrocoll 32:52–63

[26] H.N. Dengate. Swelling, pasting and gelling otf wheat starch. Adv. Cereal Sci. Technol. Vol. 6, pp. 49-82. 1984.

AUTHORS

First Author – Ansharullah Ansharullah, PhD in Food Science and Technology, Department of Food Science & Technology, Universitas Halu Oleo, Indonesia. Email: aansharullah@gmail.com.
Second Author – Sri Wahyuni. Prof. Food Science and Technology, Department of Food Science & Technology, Universitas Halu Oleo, Indonesia. Email: sriwahyuni_aan@yahoo.com.
Third Author – Muhammad Natsir. PhD in Applied Chemistry, Department of Chemistry, Universitas Halu Oleo, Indonesia.

Correspondence Author – Ansharullah Ansharullah, Department of Food Science & Technology, Universitas Halu Oleo, Indonesia. Email: aansharullah@gmail.com. Ph: +6285340521372