Research Article

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Colloidal Properties of the Rice Wine Residue of Thai Purple Rice and its Effects as a Stabilising Agent in Foams

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Abstract-Research toward food waste valorisation has been an attractive subject and aligned with the UN's Sustainable Development Goal (SDG) 12.3 aiming at drastic reduction of the ecological footprint via minimizing food losses by 2030. In this context, we draw our research focused on upcycling the rice wine residue (RWR) into a value-added ingredient. This study aimed to identify the colloidal properties of RWR and explore its potential application as a stabilising agent for foams or bubbles. Ultrasound treatment was employed at 20 kHz for 30 minutes to breakdown the rice grain and refine the particulates into smaller sizes. The particle sizes of RWR were characterized via Mastersizer and resulted in bimodal distribution with sizes of 0.12 and 27 µm. The surface net charge was found to be around -7.8 ±0.5 mV as measured via Zetasizer. The residue was dried and incorporated into a model foam system using 0.5 wt.% sodium caseinate to initiate the bubble formation. RWR at 0.5 wt.% has shown its ability to retain a stable foam over time for more than 6 hours. To conclude, RWR may potentially be deemed as a foam stabiliser via Pickering stabilization at the bubble interface.

Keywords: Rice wine residue, Thai purple berry rice, stabilizing agent, foam

1. Introduction

Foams are a biphasic system made out a liquid and gas phase where the gas contributes to the bubbles seen and the liquid usually forms a lamellar phase that coats the gas bubbles resulting in what can be generally be described as an air in water (A/W) emulsion. There are two main mechanical methods to create foams. These are bubbling in which gas is bubbled through a liquid and stirring where the gas is incorporated into the liquid by mechanically mixing, whipping or shaking. There are many factors that can impact foam stability due to the inherent unstable nature of foams. Various methods can be employed to improve the stability of foams such as increasing the viscosity of the liquid phase (Ellis *et al*., 2017). Use of inorganic particles to stabilise foams are widely researched and understood such as the use of silica particles nanoparticles (Binks & Horozov, 2005). Recently there has been increasing research in the use of particles whose origins are biological in nature so as to incorporate them into medical or food applications. There are two main groups of particles: polysaccharides (e.g. starch and cellulose) which also stabilise foams through fibre entanglement and polypeptides (e.g. soy protein and ferritin) due to their amphiphilic nature (Lam *et al*., 2014). Particles can also help stabilise foams due to Pickering stabilisation. The general theory of this mechanism is that particles would adsorb at the interface of foam or emulsion systems and form a barrier based on stearic effects, thus preventing the phase separation (Monégier du Sorbier *et al*., 2015). Pickering stabilisation using natural-origin particles has some advantages over conventional stabilising particles aforementioned above as the current consumer demand for clean label is uprising. Thus, this study will help to shed the light in exploring other natural resources for potential Pickering stabilizers in food systems, particularly in foam matrices.

Research into the valorisation of food waste or by-products created as a result of food production has seen a recent increase in the fight against food waste and increased awareness of potential environmental impacts of the discharge of waste products. One area of interest would be the waste products generated by the alcoholic beverage industry. Large amounts of wastes are generated through the brewing of wines, beers and spirits which can be seen in studies done by Guilbert and Gontard (2005) for beer and Zacharof (2016) for wine for example. The bulk of the wastes generated are solid waste residues from the filtering and clarification of the beverages. The solid wastes are usually either discarded or used in animal feed and fertilisers (Jain & Anal, 2017). There are numerous untapped or not well researched uses of the solid waste residue generated through brewing or fermenting of alcoholic beverages (Ravindran & Jaiswal, 2016). One area of interest would be the use of the residue as a stabilising agent for foams as there is little research done in this area. Thus, this study is aimed to explore the colloidal properties of RWR for its possibility to be utilized as Pickering partices and its effects as a stabilising agent in foams. It is a worthwhile effort to increase the portfolio of natural substances as stabilizing agents while converting the waste stream into value-added ingredients.

2. Materials and Methods

2.1 Materials

Two types of rice Thai glutinous rice (Green Dragon, UK) and purple rice (Thai Suwan Riceberry Brand, Thailand) was tested. Dry red rice koji (Golden Lily, China) was used to simulate the rice wine fermentation. All were used directly from the package without further chemical treatment or purification. Foam stability testing was carried out using sodium caseinate (Sigma Aldrich, United Kingdom).

2.2 Sample Preparation of RWR Particles

The Thai glutinous rice and purple rice were first washed using water in a bowl to remove any dirt or impurities from the rice and the cooked. Cooking of rice was done using steaming under retort at 121 ^{o}C, 10 psi for 35 minutes. The ratio of rice to water by weight used for the cooking process was found to be 1:1 for glutinous rice and 1:1.5 for purple rice based on literature values (Okabe, 1979 ; Chatthongpisut *et al*., 2015). The cooking time for glutinous rice and purple rice were around 32 and 35 minutes, respectively. These values also corroborate with the cooking time reported values by Nawaz *et al*. (2016) and Gaewsondee and Duangkhamchan (2019) for glutinous rice and purple rice respectively. Ranghino's method was used to determine the end point of fully-cooked rice. The rice was cooled to around 20-24 ^{o}C before being mixing with dry red rice koji which was previously ground for 30s using a grinder (Krups F2034251, Germany) with a particle size mainly 250 µm as measured via Endercott's sieves. The ratio of ground culture grains to cooked rice used was 1:4 by weight. The mixture was placed in closed jars and placed into an incubator (IVYX Scientific, USA) at 23 ^{o}C for up to 7 weeks, to mimic rice wine fermentation process following a study by Liu *et al*. (2014). The residue obtained was pressed and filtered using a cheese press through a 37 micron cheese cloth (IvyH, United Kingdom) at 20 psi for 45 min to remove large particulates. Ultrasound treatment was also used to further breakdown the particles by exposing the samples in an ultrasound tank for 20, 30 and 40 minutes at 20 kHz. Further particle separation was also performed via centrifugation at 4000 Rpm for 20 min (Eppendorf 5810R, Germany) with temperature maintained at 23 ^{o}C. The sediment was collected and dried at 30 ^{o}c for 18 H (Memmert Drying Oven, Germany) to remove excess moisture, i.e. 90 wt.% moisture was removed. The overall processing steps are summarized in (Figure 1).

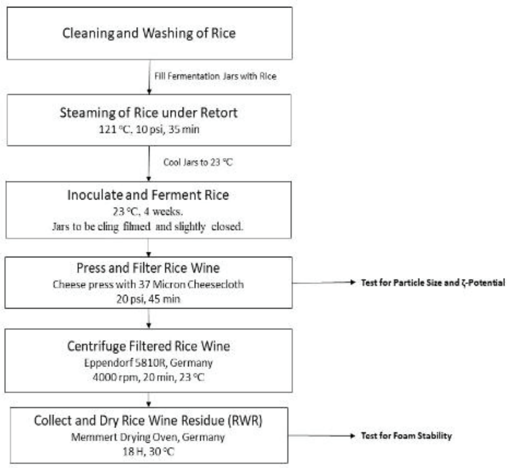


Figure 1. A schematic diagram to illustrate the processing steps in sample preparation of RWR

2.3 Particle size and ζ-potential Measurements

Particle sizes of the rice wine residue was measured using the Malvern Mastersizer 3000 (Malvern Instruments Ltd, United Kingdom) by dispersing the 0.3 g of the rice samples into 400 ml distilled water before inserting the Hydro EV probe attachment of the Malvern Mastersizer 3000. The samples were placed into disposable PMMA cuvettes and the particle sizes were measured at 25 ^{o}C. The wavelength of the laser source was at 633 nm and the light scattering was detected at 173o. Experiments were done in triplicate.

The ζ-potential was measured using the Zetasizer Nano ZS (Malvern Instruments, United Kingdom) by diluting 1:50 volume ratio of the rice samples into Millipore water at pH near 7. The Millipore water was purified using a MilliQ apparatus (Millipore, Bedford, UK) with a resistivity not less than 18.2 MW before being injected into a DTS 1061 folded capillary cells (Malvern Instruments, United Kingdom). Diluted samples were filtered using a 1 µm syringe filter, Puradisc (Whatman, United Kingdom) to remove any large aggregate particles or dust. Presence of large particles can affect the size distribution and particle mobility, because they restrict the free diffusion pattern of the target particle of interest, otherwise a biased value could have been reported.

2.4 Measurement of Foam Stability

A solution of 0.5 wt.% sodium caseinate (Sigma Aldrich, UK) was prepared to initiate the foam formation. Sodium caseinate is able to form a foam under agitation easily, however it has a poor foam stability performance on its own (Sanchez & Patino, 2005). Thus, it serves as a good foaming agent candidate to determine the effect of RWR particles in exerting foam stability. 0.5 wt.% sodium caseinate solution was prepared and heated at 40 ^{o}C using an Arex digital hotplate (VELP Scientifica, Italy) and a magnetic stirrer bar for 1.5 hours at 600 rpm then cooled to ambient temperature before use. Different concentrations of dried RWR from were tested, i.e. 0.1, 0.5 and 1 wt.% respectively, added into the sodium caseinate solution.

Foams were created by whipping the solutions above using an IKA Labortechnik Ultraturrax T25 S7 (Janke & Kunkel GmbH & Co, Germany) for 70 seconds at 24000 rpm. The sample tubes were covered with parafilm after whipping and the height of the foam (h) was measured 2 min after whipping, every 20 min for 2 hours 20 min, then at 6 and 12 hours. The initial height of the solutions prior to whipping was at 2 cm. To calculate foam volume (V), the formula in Equation (1) was used:

Equation 1. $$V\text{-}\pi r^2 h \qquad (1)$$

In Equation (1), *h* is the height of the foam and r is the radius of the test tube which was found to be 1.15 cm.

Percentage overrun of the foam can then be calculated for each time interval using the following Equation (2) below as adapted from (Raymundo *et al*., 1998), where *Vf* represents the volume of foam at a specific time interval and *Vi* represents the initial volume of solution before whipping.

Equation 2.

$$\text{Percentage Overrram} = \frac{(Vf-Vi)}{Vi} \times 100 \qquad (2)$$

To further quantify the stability of the foam produced, a graph of foam decay over time was plotted. The graph of this is better able to highlight the rate of foam decay over time.

3. Results and Discussion

Particle sizes and net surface charge are characterized for RWR particles to obtain a good understanding about the physical properties and relate them with their ability to stabilize the foam which will be discussed in the following sections.

3.1 Particle size distribution of rice wine residue

(Figure 2) shows the particle size distribution of RWR from both glutinous and purple rice samples. The results showed that RWR particles found in purple rice had bimodal distribution of particle size whereas glutinous rice had a unimodal curve. The residue obtained from fermented glutinous rice had an average particle size of 22.8 µm, while purple rice had yielded an average particle size of 0.1 and 25.7 µm. Bimodal distribution of particle size observed in purple rice samples could be attributed to the fact that purple rice contains both amylose and amylopectin whilst glutinous rice is primarily amylopectin (Wani *et al*., 2012). The purple berry rice (Riceberry) used in this study is a non-waxy rice with amylose content at around 14 % as reported by Ratseewo *et al*. (2019). While, glutinous rice is known for as sticky or waxy rice which is literally amylose-free (i.e. 0-2 % amylose, depending on cultivars as reported by Wani *et al*., 2012). The uniformity of the size in RWR of glutinous rice could be attributed to the unimodal composition of amylopectin, while the bimodal particle size distribution in purple rice was attributed to the bimodal composition of amylose and amylopectin.

When the purple RWR was subjected to sonication, there was no changes in average particle sizes, i.e. RWR ultrasound treated purple rice sample had an average particle size 0.1 and 24.2 µm. Ultrasound treatment is commonly used to reduce particles via microscopic local heating and cavitation processes in situ. However, this observation was not apparent in this study, i.e. the size changes between sonicated vs un-sonicated samples were not significantly different, $p>0.05$. Higher amylose with linear structure of α-1,4-glucopyranosyl is associated with higher crystallinity (Atkin *et al*., 1999). This may in turn provides a higher degree of resistance toward the acoustic cavitation, thus particle reduction was not observed.

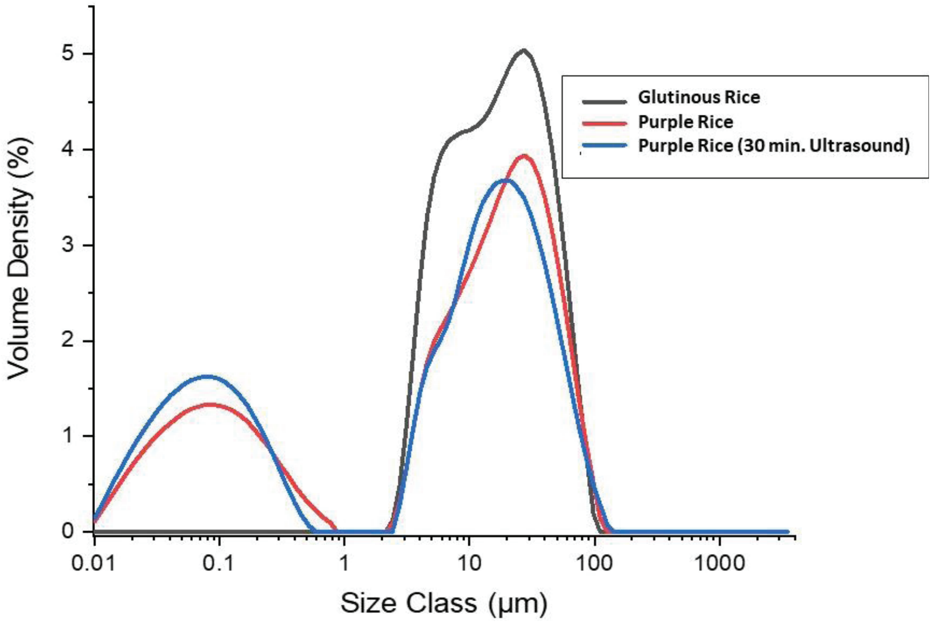


Figure 2. Particle size distribution for the rice wine residue obtained from glutinous and purple rice samples

3.2 Surface Charge (ζ-potential) Properties of Rice Wine Residue

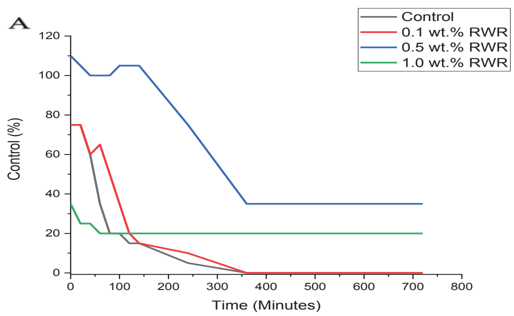
Foam is an inherently thermodynamically unstable system (Bartell, 1958). This is due to the liquid phase slowly draining out from the air and water interphase, thus causing the collapse of the bubbles in the foam resulting in foam instability (Embley & Grassia, 2006). Pickering stabilisation is one of the methods used to stabilize foams. This method utilizes solid to semi solid particles to prevent coalescence of droplets in the system and the collapse of the bubble (Horozov, 2008).

As such, the focus would be to determine if the ζ-potential values obtained can be correlated to actual foam stability due to the potential of low ζ-potential particles as a foam stabiliser and the ideal concentration of RWR to be used as a foam stabiliser. The ζ-potential measurement is used to determine the net surface charge of particles at the slipping plane based on electrophoretic mobility which based on Laser Doppler velocimetry. It is a common benchmark in colloidal system to associate the ζ-potential values with the emulsion stability. A high ζ-potential (≥ ±40 mV) indicates that the emulsion is stabilized via electrostatic repulsion, thus particles tend to stay apart from each other and flocculation or coagulation are less likely to occur (Huo *et al.*, 2019). However, this may not be applicable for Pickering particles, the ζ-potential may varied depending the mechanism of stabilization either via electrostatic forces as the particles adhere at the interface or possibly steric hindrance of large particles stabilizing the system. Regardless whichever mechanism to be proposed, essentially having the knowledge about the ζ-potential would help to postulate the possible interactions.

In this study, the ζ-potential of rice wine residue of purple rice and glutinous rice were measured. The RWR of purple rice was measured, but unsuccessful attempts for glutinous rice. The ζ-potential of residue glutinous rice was not readable because of the unimodal presence of large particles with sizes > 1 μm as seen in Figure 2. Filtration via 1 μm syringe filter Puradisc aided the removal of these large particles because otherwise the electrophoretic mobility would be hindered. The successful reading for RWR purple rice was due to the presence of small particles in the region of 0.1 μm and thus Brownian motion and inter-particle charge interaction allows the electrophoretic mobility to proceed. A surface charge of -7.8 mV (SD.±0.467) was detected for RWR purple rice and the reported value for sodium caseinate at pH 6.7 was at -17 mV (Lo *et al*., 2019). Thus, foam instability due to charge contrast could potentially be eliminated. Both systems have considerably low ζ-potential which could potentially be favourable for its likelihood to form a closely packed particle network at the interfaces of air or liquid and thus bubbles are stabilized (Huo *et al*., 2019).

3.3 Application of Rice Wine Residue (RWR) a Foam System

Overrun test is commonly done to determine foam stability over a period of time. Over or under whipped foams can have an effect the amount of air incorporated into foams as well as liquid drainage, thus affecting foam overrun percentage values (Jakubczyk & Niranjan, 2006). In this study, whipping was carefully controlled at certain rpm and timing. In addition, the foam stability tests were performed in a model system using 0.5 wt.% sodium caseinate solution to initiate the foam formation with consequent RWR at 0.1, 0.5, and 1 wt.% were added into the system to determine its impact in generating stable foams. Figure 3A showed that for a 0.5 wt.% sodium caseinate solution with addition of 0.5 wt.% RWR had the best foam forming and stabilising properties. The initial foam overrun was 110% for 0.5 wt.% concentration as compared to 75% overrun in control (i.e. no RWR) and 0.1 wt.% RWR samples. While, the least performing sample was addition of 1.0 wt.% RWR with only 35% overrun.



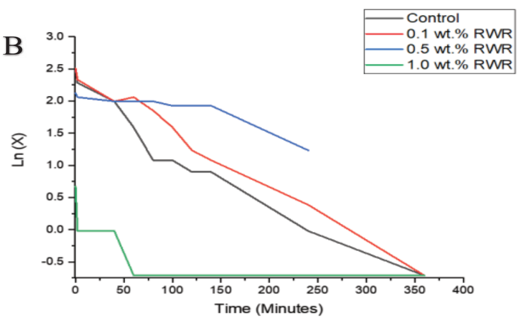


Figure 3. A) Plot of percentage overrun over time of sodium caseinate foam with addition of RWR at 0.1, 0.5 and 1 wt. % and Control with no RWR added. B) A logarithmic plot of the decrease of foam volumes over time.

The graph in Figure 3B plotted the logarithmic scale of overrun to depict the effect of the particles on the foam by relating the decrease of foam volume as a function of time based on equations by Hackbarth (2006). The graph shows a steep downward gradient for the control, 0.1 and 1 wt.% samples, which indicates the rapid decrease in the foam volume. While 0.5 wt.% RWR foam has the least steep indicating the most stable foam over time which could be attributed to the 0.5 wt.% RWR addition. Adding RWR at the right concentration in stabilizing the foam may be related to the effective concentration forming the close network at the interface. The foam instability at 0.1 wt.% RWR could be postulated due to insufficient particles populated at the interface, and vice versa it was overpopulated at 1 wt.% and forming aggregates among themselves as seen as a sediment in (Figure 4). These aggregates or large particles had caused the foam to destabilize rather than being adsorbed at the air/water interface and thus led to liquid drainage (Fameau & Salonen, 2014).

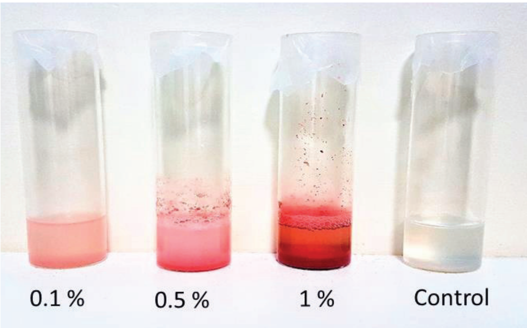


Figure 4. Images of sodium caseinate foams with RWR addition (From left to right: 0.1 wt.%, 0.5 wt.%, 1 wt.%, Control – 0 % RWR) after 12 hours storage time.

4. Conclusion

In conclusion, the RWR particulates as small as 0.1 μm were found in purple rice. Ultrasound treatment did not aid further particle reduction which could be postulated due to the higher degree of crystallinity from the amylose in purple rice. The ζ-potential measurements also support the use of the fine particulate as a foam stabiliser as the surface charge of the particulates found was to be at an ideal range, i.e. less than 40 mV. Thus, less repulsion forces could be exerted at the air/water interface causing the particles to be closely packed and stabilizing the foams. 0.5 wt.% RWR purple berry was found to be the optimum concentration in generating above 100% overrun and maintaining the foam volume higher than Control (no RWR) up to 12 hours. Future works may include further developments of this ingredient for various applications in a real food foam system rather than using sodium caseinate model system. Moreover, the potential of upcycling the waste stream from fermented rice or possibly extended to other processed rice is an area worth exploring and researching into to achieve sustainable food production.

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