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# Investigating the Malting Suitability and Brewing Quality of Different Rice Cultivars

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**Abstract:** Nineteen globally diverse rice cultivars were analyzed for various chemical parameters important to malting, including germination energy, protein, apparent amylose content, and gelatinization temperatures (GT). The rice cultivars were then malted, and congress mashes were produced. Several parameters important to brewing were then assessed in the malts and worts (i.e., extract, soluble protein, free amino nitrogen (FAN), GT, etc.). The rice malts produced were saccharified to varying degrees, had high limit dextrinase activities, and contained sufficient FAN/protein concentrations. This suggests their potential to yield robust fermentations in beer styles with high adjunct inclusions without requiring additional nitrogen supplementation. Rice cultivars with purple-pigmented bran were found to yield unique wort colors and could serve as novel natural gluten-free colorants for future recipes. Overall, these findings suggest that malted rice could offer a more local and gluten-free source of starch for brewers and beverage/food producers.

**Keywords:** rice varieties; malt; rice malt; gluten free; beer



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## 1. Introduction

Climate change [1] and international hostilities [2] are leading to a shortage of raw materials for brewing and are causing a subsequent increase in the cost of some ingredients, especially malting barley. Access to essential raw materials needed for beverage/ beer production (i.e., hops and grains like barley or wheat) will vary in availability and quality in the coming decades [3]. For example, although malted barley has been traditionally used as the main source of starch for brewing, malting barley prices in the United States have increased up to 63% in the last four years [4] due to these global pressures, and models project that barley yields will continue to be heavily impacted by climate change [5,6].

Rice (*Oryza sativa* L.) is a globally important food staple. In 2022, 512 million metric tons of rice were produced throughout the world, with the United States accounting for ~1.0% [7]. In the U.S., most rice is grown in the southern states; for example, Arkansas alone accounts for ~40% of all US rice [8]. Compared to barley, models predict that rice yields might be less impacted by climate change [9]. Therefore, by offering a more locally sourced grain, despite paddy rice being proportionally more $CO_2$ intensive to grow than malting barley [10,11], the lack of international shipping may potentially make up the difference in $CO_2$. Additionally, rice is a gluten-free source of starch for brewers and beverage/food producers.

Like barley, rice starch is comprised of amylose and amylopectin. Depending on the market class and rice cultivar, the contents of these can vary significantly [12]. For example, the apparent amylose content in rice typically ranges from 0% to 28% but can reach up to 64.8% in genetically modified cultivars [13]. A crucial feature of grain quality to consider during brewing is gelatinization temperature, which is defined as the temperature at which starch granules swell, pseudo-crystalline regions of amylopectin are melted, and amylose chains are dispersed into the medium [14]. This results in the starch losing its ordered structure, so that it can be more readily accessed and hydrolyzed by starch-degrading enzymes during the brewing process. The gelatinization temperature of grains is heavily influenced by starch properties as well as lipid and protein contents [14]. The reported [14,15] range of gelatinization temperature in malted barley is 54.5–67 °C. In comparison, a wider and higher range (62–85 °C) of gelatinization temperatures has been reported for different rice cultivars [16–20]. Due to these relatively higher gelatinization temperatures, brewers would need to modify their equipment and/or process to incorporate rice into their recipes.

The generation of fermentable sugars produced due to enzyme hydrolysis in malted grains during mashing is a critical consideration for brewers as it impacts brewing efficiency [16]. Generally, barley has been preferred as a brewing raw material due to its ability to produce starch-degrading enzymes, namely α-amylase and β-amylase, throughout the malting process. When considering germination and malting rice, Usansa, Burberg, Geiger, Back, Wanapu, Arendt, Kreisz, Boonkerd, Teaumroong, and Zarnkow [19] studied two black bran rice cultivars (6.78% and 22.2% apparent amylose) and identified that β-amylase activity in rice malt was lower than in barley malt, but higher amounts of limit dextrinase and α-glucosidase were enough to fully saccharify the starch in the rice malt. Mayer, Marconi, Regnicoli, Perretti, and Fantozzi [21] explored the benefits of using malted rice and optimized malting conditions using 10 rice cultivars grown in Italy (ranging from 16.3–26.5% amylose) and found that there was enough diastatic power to saccharify the wort made only with rice malt without needing exogenous enzymes. Ceccaroni, Marconi, Sileoni, Wray, and Perretti [22] further improved rice malting conditions and then demonstrated the performance of rice malt in a successful brewing trial. Overall, these studies highlight the potential of malted rice in brewing, but very limited data exist on the malting performance of different rice cultivars having differing starch qualities and sizes, and no information exists on the malting performance of U.S. rice varieties.

Therefore, the objective of this study was to evaluate a larger set of rice cultivars from different countries (especially important U.S. cultivars) which had a much broader range of attributes than what has been previously measured in the literature (e.g., grain size, aromatic and non-aromatic, red and purple brans, and a hybrid cultivar). The samples collected were malted using previously optimized rice malting parameters [21,22]. The malting and brewing suitability of these malts were then determined using established analytical approaches common to the brewing industry.

## 2. Materials and Methods

### *2.1. Rice Samples*

A total of 20 paddy rice samples cultivated in the southern United States and harvested between 2020 and 2022 were procured (Table 1) from Parish Rice, the USDA Dale Bumpers National Rice Research Center, and the University of Arkansas Rice Research and Extension Center. All collection procedures and methods of analysis were carried out under relevant institutional, national, and international guidelines and legislation guidelines. The 19 rice cultivars studied were genetically diverse, developed by rice breeding programs in the USA (15), Philippines (2), Brazil (1), and Japan (1), and included one commercial US hybrid cultivar, with all others being pureline cultivars, including one from a different year and growing location. Paddy rice samples were dried to 11 ± 1% moisture (wet basis) and then analyzed under similar conditions as established for barley (Table 1).

**Table 1.** Physicochemical attributes of paddy rice sorted by whole kernel length to width ratio.

| Cultivar | Characteristics and Country of Origin | Harvest Year | Whole Kernel Length/Width * (mm) | USDA Classification [23] | Chalkiness * (%) | TKW $ (g dm) | GE Aubry 3rd Day $ (%) | GE Aubry 5th Day $ (%) | Protein $ (Dumas, g/100 g d.m.) | Apparent Amylose Content @ (%) | To @ (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14 | Non-aromatic, Japan | 2022 | 1.74 | Short grain | 3.84 | 21.80 | 9.00 | 42.00 | 8.63 | 10.97 | 64.93 |
| 13 | Non-aromatic, USA | 2022 | 1.98 | Short grain | 20.62 | 19.80 | 5.00 | 35.00 | 8.09 | 11.06 | 63.59 |
| 18 | Non-aromatic, USA | 2022 | 2.15 | Medium grain | 4.46 | 24.40 | 90.00 | 92.00 | 8.93 | 10.86 | 65.58 |
| 17 | Non-aromatic, USA | 2022 | 2.51 | Medium grain | 5.02 | 19.30 | 65.00 | 79.00 | 9.58 | 10.55 | 64.71 |
| 3 | Purple bran, aromatic, Brazil | 2022 | 2.53 | Medium grain | 0.02 | 15.40 | 6.00 | 69.00 | 9.76 | 9.46 | 65.22 |
| 4 | Highly resistant starch, non-aromatic, the Philippines | 2022 | 2.72 | Medium grain | 21.49 | 16.20 | 81.00 | 85.00 | 8.57 | 26.63 | 68.28 |
| 6 | Purple bran, aromatic, USA | 2022 | 2.96 | Medium grain | 0.01 | 16.90 | 84.00 | 89.00 | 9.58 | 17.84 | 74.60 |
| 10 | Purple bran, non-aromatic, the Philippines | 2021 | 2.99 | Medium grain | 6.58 | 19.70 | 95.00 | 97.00 | 7.85 | 2.28 | 76.31 |
| 11 | Non-aromatic, USA | 2021 | 3.04 | Long grain | 87.17 | 21.60 | 95.00 | 97.00 | 8.98 | 1.72 | 65.10 |
| 9 | Non-aromatic, USA | 2022 | 3.13 | Long grain | 3.42 | 20.10 | 77.00 | 83.00 | 9.76 | 8.32 | 76.40 |
| 2 | Aromatic, USA | 2022 | 3.13 | Long grain | 3.18 | 21.70 | 84.00 | 92.00 | 9.52 | 9.22 | 64.39 |
| 8 | Hybrid, non-aromatic, USA | 2022 | 3.15 | Long grain | 16.3 | 21.30 | 96.00 | 97.00 | 8.09 | 16.02 | 73.48 |
| 12 | Red bran, non-aromatic, USA | 2022 | 3.16 | Long grain | 3.08 | 23.40 | 93.00 | 95.00 | 10.53 | 16.02 | 71.30 |
| 1 | Non-aromatic, USA | 2022 | 3.19 | Long grain | 20.1 | 21.60 | 93.00 | 95.00 | 8.03 | 15.39 | 74.57 |
| 19_2 | Aromatic, USA | 2021 | 3.22 | Long grain | 2.93 | 22.90 | 91.00 | 93.00 | 7.97 | 12.82 | 65.74 |
| 7 | Aromatic, the Philippines | 2020 | 3.25 | Long grain | 0.9 | 22.70 | 93.00 | 95.00 | 6.96 | 10.52 | 65.13 |
| 19_1 | Aromatic, USA | 2022 | 3.39 | Long grain | 1.39 | 20.10 | 74.00 | 78.00 | 9.94 | 11.58 | 65.07 |
| 16 | Non-aromatic, USA | 2022 | 3.41 | Long grain | 9.99 | 19.10 | 81.00 | 87.00 | 9.70 | 17.46 | 70.65 |
| 5 | Aromatic, USA | 2022 | 3.48 | Long grain | 1.97 | 22.60 | 92.00 | 95.00 | 9.76 | 21.99 | 71.80 |
| 15 | Non-aromatic, USA | 2022 | 3.52 | Long grain | 9.32 | 19.10 | 90.00 | 92.00 | 8.09 | 17.59 | 73.07 |
| $\hat{r}$ | | | 0.04 | | 0.36 | 1.1 | $1.5 \times (100\text{-m})^{0.5}$ # | $1.4 \times (100\text{-m})^{0.5}$ # | 0.063 | 1.86 | 0.55 |

* Measurement performed using milled rice. $ Measurement performed using paddy rice. @ Measurement performed using dehusked paddy (brown) rice. TKW—thousand kernel weight (g dm, dry matter), GE Aubry—germination energy by Aubry method, To—onset gelatinization temperature. Values are expressed as a mean ($n$ = 2). $\hat{r}$ is the 95% repeatability coefficient of the method or 2.77 × ($s_w$, the within-subject standard deviation). # m represents the mean. Colors represent increasing amount; light green low amount and dark green high amount.

Paddy rice samples were analyzed for the following attributes: grain moisture (dry basis) according to EBC 3.2, thousand kernel weight (TKW) according to EBC 3.4, and total nitrogen according to EBC 3.3.2 [23]. Total protein content was calculated from the total nitrogen content with a conversion factor of 5.95. Moreover, germinative energy was determined using the Aubry method, germination temperature was adjusted to 28 °C according to EBC 3.6.1 [23], and water sensitivity was determined according to MEBAK R-110.34.612 2016-03 [24], but the temperature was adjusted to 28 °C based on previous studies [22]. Based on the results from EBC 3.6.1, the germinative energy after three and five days in a 4 mL Petri dish was calculated and additionally determined.

Whole kernel rice grain parameters (length, width, length to width ratio, and chalkiness) were obtained using Vibe QM3 Rice Analyzer (Vibe, Capitola, CA, USA) in milled rice. The paddy rice samples were cleaned using a dockage tester (XT4, Carter Day, Minneapolis, MN, USA). The cleaned paddy rice samples were conditioned to 12.5 ± 0.5% moisture content (wet basis) using gentle natural air drying in an environment-controlled chamber (25 °C air temperature, 56% air relative humidity). The moisture content was measured using the moisture content meter (AM 5200–A, PerkinElmer, Boston, MA, USA). The dried samples were dehulled using a dehuller (THU35A, Satake Engineering, Tokyo, Japan) and then milled using a laboratory mill (McGill Number 2, Rapsco, Brookshire, TX, USA) for 30 s to achieve a surface lipid content of 0.4 ± 0.1%. The separation between the head rice and the broken rice was performed using a grain sieve shaker (RX-29, RO-TAP, Mentor, OH, USA).

For the apparent amylose content and gelatinization properties, paddy rice was dehusked and ground, according to published methods. The paddy rice was dehusked using a laboratory sheller (THU 35A, Satake Engineering Co., Tokyo, Japan). The apparent amylose content was determined by colorimetric assay, as performed by Juliano [25], and measured in a UV-visible spectrophotometer (Pharmaspec UV-1700, Shimadzu, Kyoto, Japan) at 620 nm. The gelatinization properties were measured using a differential scanning calorimeter (DSC, model 4000, PerkinElmer, Boston, MA, USA) based on Patindol, Jinn, Wang, and Siebenmorgen [20] Eight mg of rice flour were weighed into a stainless-steel pan and 16 µL of DI water added. The hermetically sealed pan was equilibrated for one hour at room temperature before DSC scanning from 25 °C to 125 °C at a rate of 5 °C/min. The onset gelatinization temperature (To), peak gelatinization temperature (Tp), and end gelatinization temperature (Te) were obtained with Pyris data analysis software (PerkinElmer Inc., Boston, MA, USA, version 11.1).

### 2.2. Micro Malting

Steeping and malting of the paddy rice was performed on a Heil small-scale malting system at the VLB facilities (Berlin, Germany) as described by Müller, Kleinwaechter, Selmar, and Methner [26].

Preliminary malting trials were performed with sample #19_2 to test the previously reported optimized malting conditions [21,22] for the rice varieties used and by utilizing the specific equipment employed for the malting trials in this study (Supplementary Materials—pre-trial data with 19_2). Additionally, β-glucan was measured in the preliminary trials. In agreement with past studies [19,21,22], β-glucan was below the limit of detection (<50 mg/L, calcofluor method) (Supplementary Materials—pre-trial with 19_2), so it was not assessed in any of the subsequent rice samples. After these preliminary trials, the 20 rice samples were malted, congress mashes were made, and simulated boiling trials were performed (see Section 2.3). Subsequently, the rice malts and worts produced were evaluated regarding their brewing quality (see Section 3.2). Respiration loss was calculated based on the mass of rice before malting and the mass of malted rice before cleaning. Rootlet growth loss was calculated based on the percent difference between the rootlet mass and malted rice (dry matter).

For the micro malting of rice, 900 g of paddy rice from each sample was split into two malting cylinders to provide sufficient space for rootlet growth during malting. Malting parameters were based on Ceccaroni, Marconi, Sileoni, Wray, and Perretti [22] with a minor change (Figure 1). The minor change was that the steeping temperature was set to 25 °C and maintained until the fourth and last day of wet steeping to better mimic industrial malting practices. All wet steeping rests lasted 8 h and were followed by 16 h dry steeping rests. The phase after the fourth wet steeping was regarded as the onset of the germination phase (Figure 1) and the temperature was then set to 20 °C and kept constant. Withering and kilning were performed according to Ceccaroni, Marconi, Sileoni, Wray, and Perretti [22], starting for 12 h at 45 °C, then 12 h at 50 °C, then 13.5 h at 55 °C, and finally 6 h at 70 °C. To assess drying kinetics, a third cylinder with 450 g paddy rice was malted and samples for moisture determination were taken after every temperature phase (after 12 h, 24 h, 37.5 h, and 43.5 h from the start of kilning) (Supplementary Materials—drying kinetics).

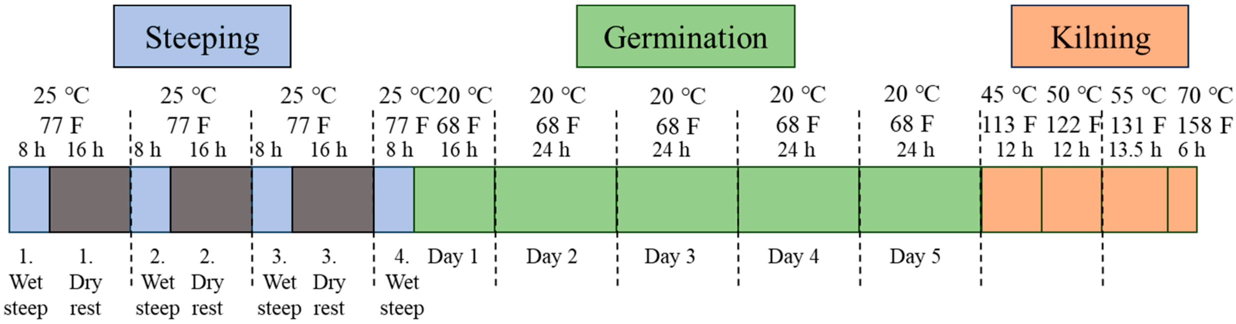


**Figure 1.** Malting scheme applied to rice samples. Dashed lines indicate 24 h periods.

After kilning, the dry and brittle rootlets were removed using a horizontal sieve shaker (type AS 400, Retsch, Haan, Germany) with a 2 mm sieve size (100 mm diameter) and three steel rings per sieve. The two malting cylinders used for each rice cultivar were then homogenized before further analysis.

### 2.3. Malted Rice Analyses

For malt analysis, a modified congress mash (EBC 4.5.1) [23] according to Mayer, Marconi, Regnicoli, Perretti, and Fantozzi [21] was applied with the addition of 10 mL $CaCl_2 \cdot 2H_2O$ at a concentration of 22 g/L and 0.144 mL of lactic acid at a concentration of 80%, and enzymatic rests were performed at 30 min at 45 °C, 30 min at 64 °C, and 30 min at 74 °C.

Malted rice quality was assessed by measuring their moisture (% dry basis) according to EBC 4.2 [23]; extract content (fine grist) according to EBC 4.5.1 [23]; viscosity (falling ball) according to EBC 4.8 [23]; saccharification of congress wort and saccharification time according to EBC 4.5.1 [23] (total observed time was 30 min due to adjustment of congress wort temperature profile); filtration behavior of congress wort according to MEBAK R-205.04.730 2016-03 [24]; apparent final attenuation according to MEBAK R-205.17.080 2016-03 [24]; photometric iodine method in wort according to MEBAK Bd. WBB 2012, Kap. 2.3 [27]; wort color (spectrophotometric) according to EBC 4.7.1 [23]; pH according to EBC 8.17 [23]; diastatic power according to EBC 4.12 [23]; α- and β-amylase activity (Megazyme, Bray, Ireland) according to MEBAK R-200.24.111 2016-03 [24] and MEBAK R-200.22.111 2016-03 [24], respectively; protein content (Dumas) according to EBC 4.3.2; [23] soluble nitrogen (Dumas) according to EBC 4.9.3 [23]; Kolbach index (Dumas) according to EBC 4.9.1 [23]; and α-amino nitrogen (ninhydrin method) according to EBC 4.10 [23].

Apparent amylose content and gelatinization properties in malt were measured using the same methods already described for the evaluation of paddy rice; however, before analysis, the malt was reconditioned to approximate 10% moisture. To estimate the impact of the different starch degrading enzymes on the gelatinization profile, DSC scanning was performed from 25 °C to 125 °C at a rate of 5 °C/min with a 30 min rest at 40 °C, 45 °C, 50 °C, 55 °C, 60 °C, and 65 °C, as well as a run with both a 30 min rest at 55 °C and then another 30 min rest at 65 °C. Amyloglucosidase was extracted according to Usansa, Burberg, Geiger, Back, Wanapu, Arendt, Kreisz, Boonkerd, Teaumroong, and Zarnkow [19], and limit dextrinase was extracted using an assay kit (Megazyme, Bray, Ireland) [28]. Enzyme activities for amyloglucosidase and limit dextrinase were measured using Megazyme assay kits, R-AMG3 and K-PullG6, respectively [28].

### *2.4. Statistical Analyses*

Statistical analyses (e.g., Pearson's correlations and principal component analysis) as well as graphical analyses were performed with Excel 2019 (Microsoft, Redmond, WA, USA) using XLSTAT Premium 2021.3.1 (Addinsoft, Long Island City, NY, USA). Repeatability (r—the 95% repeatability coefficient) was calculated as $r = 1.96 \times \sqrt{2s_w^2}$ (or 2.77×s) for apparent amylose content, gelatinization temperatures (onset, peak, and end), as well as enzymes (α-amylase, β-amylase, limit dextrinase, amyloglucosidase, and α-glucosidase), for other measurements, repeatability was as stated on MEBAK [24]. These values are used on the graphs as error bars to represent the significant differences between the samples.

## 3. Results and Discussion

### *3.1. Paddy Rice Quality Characteristics*

#### 3.1.1. General Seed and Malting Qualities

The thousand kernel weights of the rice cultivars were between 17.4 g and 27.6 g (Table 1). This finding is similar to paddy rice reported by others [21,29], with the values being almost half that of barley [30]. The lower values of rice compared to barley were expected due to botanical differences (i.e., grain length, grain width, and grain thickness) [31] between the species, as barley kernels are typically larger. The USDA [32] characterizes rice as short (<2.0 mm), medium (2.1–3.0 mm), or long (>3.1 mm) grain according to length to width ratio of the rice. Rice dimensions ranged from 4.73 to 7.02 mm in length, 1.85 to 2.74 mm in width, and 1.74 to 3.52 mm in length/width ratio (Table 1 and Supplementary Materials—correlation data). Whole kernel chalky percentage ranged from 0.01 to 87.17% (Table 1). Chalkiness affects rice pricing and can decrease the price of rice from 30% to 50% [10]. Total protein content ranged from 7.0% to 10.5%, which was greater than that previously reported in other rice malting studies [21,22,33], and some of the rice cultivars had protein contents comparable to malting barley [30].

Germinative energy (GE) is the percentage of paddy rice kernels that germinate in three days after being hydrated and is considered acceptable if more than 90% of the grains germinate and ideal if over 95% germinate. GE was measured as ideal (>95%) after the third day for three cultivars (#8, #10, and #11), as shown in Table 1. After the fifth day of germination, GE was acceptable for 11 cultivars and ideal for 7 cultivars (Table 1). The upward trend in GE was true for all cultivars between the third and the fifth day of germination, surpassing a 10% increase for #3, #13, #14, and #17. This indicates that these cultivars possibly have slower water intake and/or require higher moisture content to break dormancy. Cultivar differences for hull moisture diffusivity have also been reported [34]. Additionally, GE is highly affected by age, storage conditions, and other parameters which were not controlled in this study but should be considered and investigated in future studies. GE correlated positively with whole kernel length and negatively with width ($p < 0.05$, Table 2) and, overall, the GE of the short-grain varieties was low. Interestingly, water sensitivity was negative for #1, #2, #7, #11, #14, #16, and #18 (Supplementary Materials—correlation data), indicating that germination was enhanced by excess water rather than promoting anoxia, which may be related to rice being adapted to flooded agriculture techniques.

**Table 2.** Pearson's correlations for physical and physicochemical attributes of paddy rice with malted rice and congress wort attributes. Complete table with all correlations is in Supplementary Materials—Pearson's correlation tests. Main attributes in paddy rice (gray), malted rice (blue), and congress wort (yellow) are highlighted.

| Variables | Whole Kernel Length/Width | Whole Kernel Chalky Percentage | TKW (db) | Paddy Rice Protein | GE 3rd Day | GE 5th Day | Water Sensitivity | Paddy Rice Apparent AmyloseContent | Rice Onset Gel. Temp. | Rice End Gel. Temp. | Malting Losses | Rice Malt Protein | Diastatic Power | Alpha-Amylase | Beta-Amylase | Amyloglucosidase | Limit Dextrinase | Rice Malt Apparent Amylose Content | Rice Malt Onset Gel. Temp. | Rice Malt End Gel. Temp. | Viscosity | Elapsed Time of Wort | Fine Extract | Saccharification time | Apparent Final Attenuation | Soluble Nitrogen (mg/L) | Soluble Protein (%) | FAN (mg/L) | Kolbach Index | Wort Color |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Whole Kernel Length/Width | **1** | −0.005 | 0.073 | 0.083 | **0.735** | **0.754** | 0.127 | 0.218 | **0.471** | 0.328 | **0.456** | −0.011 | 0.401 | **0.518** | 0.293 | 0.179 | −0.170 | 0.274 | 0.410 | 0.331 | −0.076 | −0.254 | −0.424 | 0.076 | 0.427 | 0.159 | 0.153 | 0.236 | 0.142 | −0.089 |
| Whole Kernel Length | **0.938** | 0.063 | 0.348 | 0.050 | **0.858** | **0.821** | −0.064 | 0.195 | 0.414 | 0.252 | 0.371 | −0.088 | 0.398 | **0.516** | 0.268 | 0.350 | −0.085 | 0.228 | 0.379 | 0.314 | −0.194 | −0.272 | −0.312 | −0.021 | **0.492** | 0.296 | 0.294 | 0.347 | 0.295 | −0.232 |
| Whole Kernel Width | **−0.903** | 0.047 | 0.299 | −0.125 | **−0.503** | **−0.610** | −0.364 | −0.173 | **−0.454** | −0.398 | −0.406 | −0.112 | −0.390 | −0.442 | −0.332 | 0.049 | 0.243 | −0.243 | −0.381 | −0.334 | −0.019 | 0.201 | **0.512** | −0.201 | −0.367 | −0.003 | 0.005 | −0.100 | 0.042 | −0.152 |
| Whole Kernel Chalky Percentage | −0.005 | **1** | 0.040 | −0.135 | 0.133 | 0.101 | −0.160 | −0.291 | −0.136 | 0.123 | 0.123 | −0.270 | 0.019 | −0.133 | −0.051 | 0.368 | −0.068 | −0.261 | −0.068 | 0.191 | 0.025 | 0.291 | 0.123 | 0.168 | 0.024 | 0.015 | 0.013 | 0.063 | 0.192 | −0.161 |
| Total Chalky Weight % | 0.015 | **0.969** | −0.041 | −0.081 | 0.165 | 0.151 | −0.174 | −0.187 | −0.165 | 0.136 | 0.128 | −0.182 | 0.049 | −0.083 | −0.004 | 0.348 | −0.010 | −0.157 | −0.069 | 0.202 | −0.025 | 0.322 | 0.108 | 0.148 | 0.139 | 0.137 | 0.134 | 0.197 | 0.232 | −0.081 |
| TKW (db) | 0.073 | 0.040 | **1** | −0.154 | 0.373 | 0.247 | **−0.463** | −0.209 | −0.129 | −0.384 | −0.128 | −0.296 | −0.110 | −0.150 | −0.230 | 0.394 | 0.247 | −0.253 | −0.147 | −0.204 | −0.103 | −0.010 | 0.336 | −0.306 | −0.032 | 0.069 | 0.079 | 0.014 | 0.236 | **−0.600** |
| Paddy Rice Protein | 0.083 | −0.135 | −0.154 | **1** | −0.085 | −0.010 | 0.196 | 0.109 | 0.012 | −0.040 | 0.036 | **0.909** | −0.138 | 0.021 | −0.070 | 0.358 | 0.364 | 0.111 | −0.038 | −0.098 | −0.333 | −0.180 | −0.040 | −0.130 | −0.195 | 0.117 | 0.120 | 0.051 | **−0.521** | 0.067 |
| Germination Energy 3rd day | **0.735** | 0.133 | 0.373 | −0.085 | **1** | **0.935** | −0.253 | 0.148 | **0.467** | 0.353 | **0.471** | −0.271 | **0.548** | **0.627** | **0.449** | 0.165 | −0.051 | 0.146 | **0.479** | **0.470** | −0.097 | −0.194 | −0.346 | −0.111 | **0.638** | **0.511** | **0.503** | **0.581** | **0.576** | −0.056 |
| Germination Energy 5th day | **0.754** | 0.101 | 0.247 | −0.010 | **0.935** | **1** | −0.206 | 0.093 | **0.453** | 0.380 | 0.429 | −0.144 | **0.562** | **0.570** | **0.478** | 0.026 | −0.023 | 0.107 | **0.447** | **0.470** | −0.078 | −0.090 | −0.407 | −0.041 | **0.648** | 0.434 | 0.427 | **0.523** | **0.470** | 0.082 |
| Water Sensitivity | 0.127 | −0.160 | **−0.463** | 0.196 | −0.253 | −0.206 | **1** | 0.083 | 0.135 | 0.193 | −0.203 | 0.402 | −0.171 | −0.016 | −0.200 | 0.053 | −0.129 | 0.101 | 0.110 | 0.055 | 0.393 | 0.112 | −0.202 | 0.076 | −0.140 | −0.181 | −0.187 | −0.193 | −0.416 | 0.105 |
| Paddy Rice Apparent Amylose Content | 0.218 | −0.291 | −0.209 | 0.109 | 0.148 | 0.093 | 0.083 | **1** | 0.227 | 0.276 | 0.215 | 0.128 | 0.190 | **0.552** | 0.183 | 0.060 | −0.194 | **0.987** | 0.279 | 0.132 | −0.175 | −0.242 | −0.244 | 0.097 | −0.002 | 0.219 | 0.211 | 0.236 | 0.051 | 0.009 |
| Paddy Rice Onset Gel. Temp. | **0.471** | −0.136 | −0.129 | 0.012 | **0.467** | **0.453** | 0.135 | 0.227 | **1** | **0.849** | 0.415 | −0.129 | **0.679** | **0.723** | **0.596** | −0.024 | **−0.515** | 0.271 | **0.971** | **0.817** | 0.150 | **−0.446** | **−0.882** | 0.314 | 0.215 | 0.313 | 0.296 | 0.366 | 0.328 | 0.240 |
| Paddy Rice Peak Gel. Temp. | 0.419 | −0.017 | −0.253 | −0.021 | **0.470** | **0.465** | 0.128 | 0.277 | **0.955** | **0.955** | **0.446** | −0.159 | **0.689** | **0.789** | **0.619** | −0.021 | **−0.557** | 0.309 | **0.984** | **0.932** | 0.150 | −0.353 | **−0.893** | 0.351 | 0.341 | 0.398 | 0.378 | **0.470** | 0.421 | 0.275 |
| Paddy Rice End Gel. Temp. | 0.328 | 0.123 | −0.384 | −0.040 | 0.353 | 0.380 | 0.193 | 0.276 | **0.849** | **1** | 0.420 | −0.150 | **0.624** | **0.772** | **0.562** | 0.021 | **−0.543** | 0.311 | **0.901** | **0.951** | 0.163 | −0.217 | **−0.843** | 0.426 | 0.331 | 0.376 | 0.359 | **0.451** | 0.412 | 0.285 |

Significant ($p < 0.05$) correlations are highlighted in bold. Positive correlations are in green and negative correlations are in red. Thousand-kernel weight dry basis (TKW (db)), germination energy (GE) on 3rd day and 5th day using Aubry method, free amino nitrogen content (FAN), and onset, peak, and end gelatinization temperatures (Gel. Temp.).

3.1.2. Starch Qualities

Starch properties (i.e., apparent amylose content as well as onset, peak, and end gelatinization temperatures) of the different rice cultivars were also evaluated (Table 1). The apparent amylose content ranged from 1.72% in #11 to 26.63% in #4. Ceppi and Brenna [29] reported a similar range of apparent amylose content in rice. Peak gelatinization temperature (Tp) ranged from 70.48 °C in #7 to 84.65 °C in #10, which is broader than the ranges determined by Usansa, Burberg, Geiger, Back, Wanapu, Arendt, Kreisz, Boonkerd, Teaumroong, and Zarnkow [19] in rice. Onset gelatinization temperatures (To) ranged from 64.39 °C to 76.40 °C. In 14 cultivars, starch gelatinization started below ~72 °C (i.e., roughly the optimum temperature to promote α-amylase activity) and 7 (#'s 2, 7, 13, 14, 17, 18, and 19_1) had Tp below this temperature. However, end gelatinization temperatures ranged from 76.78 °C to 88.23 °C. This highlights that the gelatinization temperature is higher than the optimal temperature for α- and β-amylase activities as well as other starch-degrading enzymes and why brewers need a second vessel to gelatinize adjunct rice starch before hydrolyzing the starch in the mash tun with endogenous enzymes from barley malt (traditionally, rice is used in brewing as a secondary source of starch).

Overall, in comparison to other studies [19,21,22] which have investigated the malting properties of rice, these results highlight a broader range of malting properties exist in the diverse rice cultivars evaluated in this study.

### *3.2. Malted Rice Quality Characteristics*

In comparison to barley, longer steeping times, germination times, and temperatures are needed for rice, and this promotes more rootlet growth and respiration. Generally, the malting losses observed (~15%, see Supplementary Materials—malting losses) due to respiration (~7.5%) and rootlet growth (~7.8%) were about 2–3% higher than what has been reported during the malting of barley [35]. However, malting loss could be minimized by optimizing malting for each cultivar (such as determining the optimum time, temperature, and steeping degree to maximize enzyme formation and protein degradation) rather than using the same protocol for all samples. Additionally, there is a need for future research to investigate the factors influencing malting loss in rice, such as the application of salt-conditioned water in the germination stage and/or the addition of a grain extract during the germination stage [35]. Nevertheless, since the malting qualities of U.S. rice cultivars had not yet been evaluated, the goal of this study was to use previously optimized malting conditions to identify rice cultivars with high malting potential.

3.2.1. Enzymatic Activities

Fermentable sugars are produced due to the enzymatic hydrolysis of starch in malted grains during mashing, which is a critical consideration for brewers. The diastatic power (DP) or estimate of the combined activity of α- and β-amylase of the rice malts, which is estimated iodometrically [23] was ~7.5x lower (on average ~41°WK, Figure 2A, Table 3, and Supplementary Materials—correlation data) than what has been reported for malted barley (240–400°WK) [36]. However, cultivars #1, #6, and #10 had higher DP (91, 84, and 60°WK, respectively) than previously reported for rice by Ceccaroni, Sileoni, Marconi, De Francesco, Lee, and Perretti [37] but were similar to values reported by Mayer, Marconi, Regnicoli, Perretti, and Fantozzi [21] as well as Ceppi and Brenna [29].

**Table 3.** Pearson's correlations for physicochemical attributes of malted rice with paddy rice and congress wort attributes. Complete table with all correlations is in Supplementary Materials—Pearson's correlation tests. Main attributes in paddy rice (gray), malted rice (blue), and congress wort (yellow) are highlighted.

| **Variables** | **Whole Kernel Length/Width** | **Whole Kernel Chalky Percentage** | **TKW (db)** | **Paddy Rice Protein** | **GE 3rd Day** | **GE 5th Day** | **Water Sensitivity** | **Paddy Rice Apparent AmyloseContent** | **Rice Onset Gel. Temp.** | **Rice End Gel. Temp.** | **Malting Losses** | **Rice Malt Protein** | **Diastatic Power** | **Alpha-Amylase** | **Beta-Amylase** | **Amyloglucosidase** | **Limit Dextrinase** | **Rice Malt Apparent Amylose Content** | **Rice Malt Onset Gel. Temp.** | **Rice Malt End Gel. Temp.** | **Viscosity** | **Elapsed Time of Wort** | **Fine Extract** | **Saccharification time** | **Apparent Final Attenuation** | **Soluble Nitrogen (mg/L)** | **Soluble Protein (%)** | **FAN (mg/L)** | **Kolbach Index** | **Wort Color** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Malting Losses | **0.456** | 0.123 | −0.128 | 0.036 | **0.471** | 0.429 | −0.203 | 0.215 | 0.415 | 0.420 | **1** | −0.131 | 0.432 | **0.603** | 0.303 | −0.148 | −0.034 | 0.234 | 0.417 | **0.472** | 0.236 | 0.062 | −0.289 | −0.136 | 0.310 | **0.469** | **0.454** | **0.544** | 0.436 | 0.100 |
| Malted Rice Protein | −0.011 | −0.270 | −0.296 | **0.909** | −0.271 | −0.144 | 0.402 | 0.128 | −0.129 | −0.150 | −0.131 | **1** | −0.235 | −0.109 | −0.174 | 0.199 | 0.380 | 0.137 | −0.174 | −0.243 | −0.206 | −0.012 | 0.028 | −0.209 | −0.188 | 0.061 | 0.067 | 0.000 | **−0.610** | 0.167 |
| Diastatic Power | 0.401 | 0.019 | −0.110 | −0.138 | **0.548** | **0.562** | −0.171 | 0.190 | **0.679** | **0.624** | 0.432 | −0.235 | **1** | **0.631** | **0.910** | −0.187 | −0.285 | 0.227 | **0.667** | **0.659** | −0.082 | −0.323 | **−0.628** | 0.107 | **0.534** | **0.522** | **0.514** | **0.591** | **0.600** | **0.502** |
| Alpha Amylase | **0.518** | −0.133 | −0.150 | 0.021 | **0.627** | **0.570** | −0.016 | **0.552** | **0.723** | **0.772** | **0.603** | −0.109 | **0.631** | **1** | **0.558** | 0.103 | −0.274 | **0.566** | **0.750** | **0.729** | −0.084 | −0.334 | **−0.640** | 0.156 | **0.495** | **0.608** | **0.597** | **0.652** | **0.538** | 0.155 |
| Beta Amylase | 0.293 | −0.051 | −0.230 | −0.070 | **0.449** | **0.478** | −0.200 | 0.183 | **0.596** | **0.562** | 0.303 | −0.174 | **0.910** | **0.558** | **1** | −0.234 | −0.255 | 0.224 | **0.570** | **0.553** | −0.138 | −0.338 | **−0.649** | 0.152 | 0.419 | 0.363 | 0.353 | **0.449** | 0.430 | **0.697** |
| Amyloglucosidase | 0.179 | 0.368 | 0.394 | 0.358 | 0.165 | 0.026 | 0.053 | 0.060 | −0.024 | 0.021 | −0.148 | 0.199 | −0.187 | 0.103 | −0.234 | **1** | 0.155 | 0.075 | −0.012 | 0.035 | −0.316 | −0.114 | 0.079 | 0.090 | −0.115 | 0.116 | 0.126 | 0.048 | −0.081 | **−0.541** |
| Limit dextrinase | −0.170 | −0.068 | 0.247 | 0.364 | −0.051 | −0.023 | −0.129 | −0.194 | **−0.515** | **−0.543** | −0.034 | 0.380 | −0.285 | −0.274 | −0.255 | 0.155 | **1** | −0.212 | **−0.566** | **−0.489** | −0.073 | 0.392 | **0.555** | −0.311 | 0.008 | 0.282 | 0.300 | 0.190 | −0.038 | −0.038 |
| Malted Rice Apparent Amylose Content | 0.274 | −0.261 | −0.253 | 0.111 | 0.146 | 0.107 | 0.101 | **0.987** | 0.271 | 0.311 | 0.234 | 0.137 | 0.227 | **0.566** | 0.224 | 0.075 | −0.212 | **1** | 0.305 | 0.145 | −0.164 | −0.241 | −0.306 | 0.181 | −0.030 | 0.189 | 0.182 | 0.219 | 0.023 | 0.057 |
| Rice Malt Onset Gel. Temp. | 0.410 | −0.068 | −0.147 | −0.038 | **0.479** | **0.447** | 0.110 | 0.279 | **0.971** | **0.901** | 0.417 | −0.174 | **0.667** | **0.750** | **0.570** | −0.012 | **−0.566** | 0.305 | **1** | **0.897** | 0.173 | −0.389 | **−0.878** | 0.296 | 0.300 | 0.396 | 0.376 | **0.461** | 0.421 | 0.199 |
| Rice Malt Peak Gel. Temp. | 0.382 | 0.066 | −0.188 | −0.082 | **0.505** | **0.481** | 0.071 | 0.216 | **0.902** | **0.947** | **0.465** | −0.229 | **0.666** | **0.771** | **0.573** | 0.011 | **−0.535** | 0.234 | **0.967** | **0.973** | 0.193 | −0.268 | **−0.843** | 0.296 | 0.427 | **0.469** | **0.449** | **0.547** | **0.523** | 0.202 |
| Rice Malt End Gel. Temp. | 0.331 | 0.191 | −0.204 | −0.098 | **0.470** | **0.470** | 0.055 | 0.132 | **0.817** | **0.951** | **0.472** | −0.243 | **0.659** | **0.729** | **0.553** | 0.035 | **−0.489** | 0.145 | **0.897** | **1** | 0.198 | −0.162 | **−0.790** | 0.268 | **0.477** | **0.489** | **0.470** | **0.569** | **0.569** | 0.187 |

Significant ($p < 0.05$) correlations are highlighted in bold. Positive correlations are in green and negative correlations are in red. Thousand-kernel weight dry basis (TKW (db)), germination energy (GE) on 3rd day and 5th day using Aubry method, free amino nitrogen content (FAN), and onset, peak, and end gelatinization temperatures (Gel. Temp.).

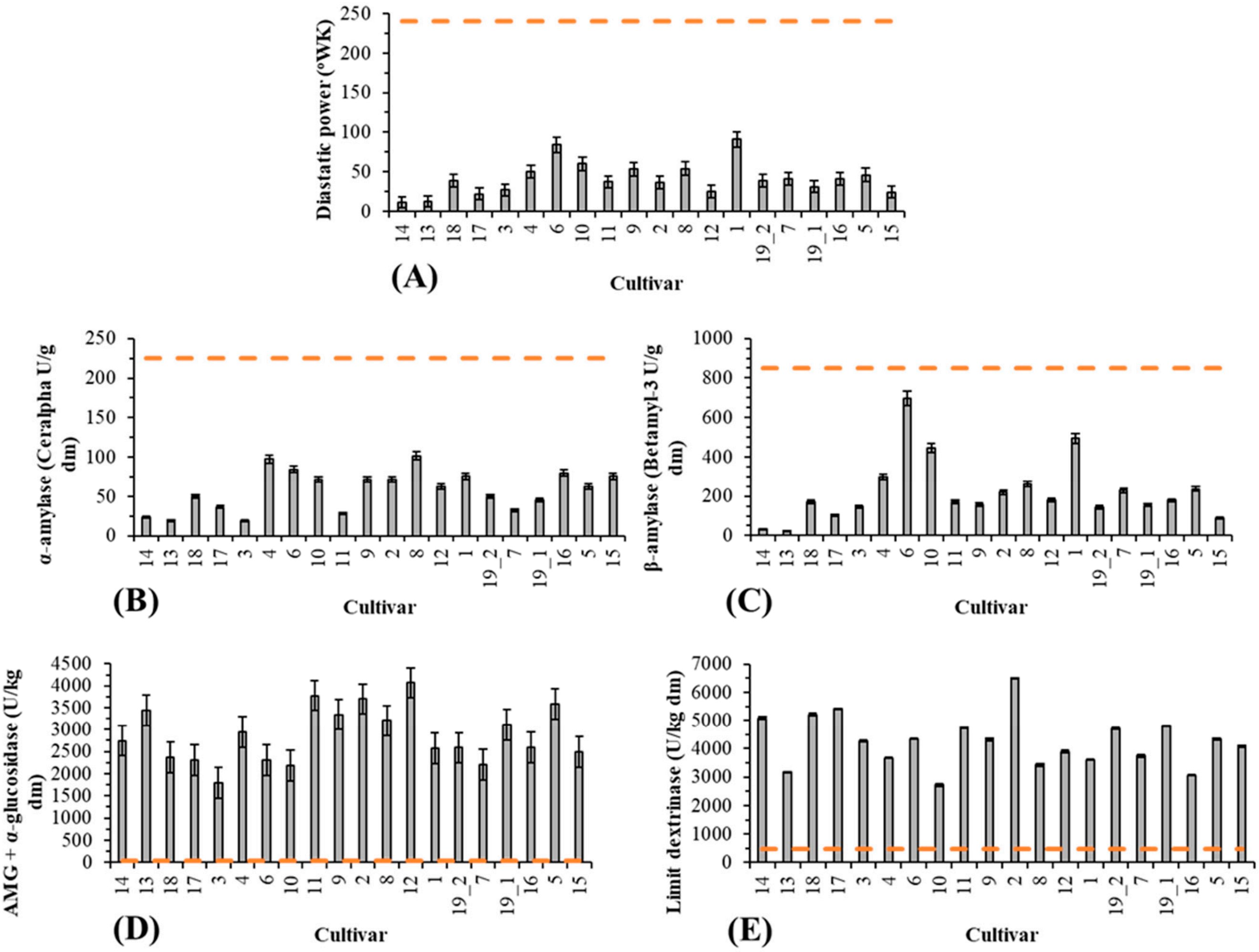


**Figure 2.** Variations in (**A**) diastatic power, (**B**) α-amylase, (**C**) β-amylase, (**D**) amyloglucosidase (AMG) + α-glucosidase, and (**E**) limit dextrinase for malted rice. Samples are sorted by length/width ratio. Orange dashed lines indicate the optimum range for barley malt [38]. Data points refer to mean values ($n$ = 2), and error bars represent r the 95% repeatability coefficient.

The major starch degrading enzymes (limit dextrinase, amyloglucosidase, β-amylase, and α-amylase) were investigated to determine the contribution of each to the diastatic power of the different rice malts produced in this study (Figure 2B–E). In agreement with the previously published results [19,21,22], the activities of limit dextrinase, amyloglucosidase, and β-amylase were among the highest measured starch degrading enzymes in the rice malts (Figure 2).

β-amylase activity was on average ~221.7 Betamyl-3 U/g dry matter (dm) and varied from 25 to 697 Betamyl-3 U/g dm (Figure 2C). Cultivars #6 (~697 Betamyl-3 U/g dm), #1 (~495 Betamyl-3 U/g dm), and #10 (~444 Betamyl-3 U/g dm) had the highest β-amylase activities among the rice malts analyzed in this study, which is in agreement with what has been previously reported [19,21,22,39]. However, the β-amylase activity in these rice malts is on the lower end of what has been reported for malted barley (600–1800 U/g) [38].

As aforementioned, α-amylase is another important enzyme in the brewing process that contributes to diastatic power. The mean α-amylase activity measured among the samples was 58 Ceralpha U/g dm (Figure 2B). Cultivars #8 and #4 had the highest α-amylase activities (102 and 97 Ceralpha U/g dm, respectively). Previous studies [19,21,22,39] have reported rice malt α-amylase activities ranging from 18.5 to 225 Ceralpha U/g, with the latter being similar to levels of α-amylase measured in malted barley [38]. As expected, the activities of α- and β-amylases of the rice malts were positively correlated with the diastatic power ($p < 0.01$, Table 3).

Limit dextrinase is a starch-debranching enzyme that cleaves amylopectin α-1-6 glycosidic bonds [19,40] and releases linear amylopectin chains. On average, the limit dextrinase activity in the rice malts was 4255 U/kg dm; this is ~6x times higher than the limit dextrinase activity reported in barley (349–800 U/kg) [16,19,41,42]. The highest activities were found in cultivars #2 (6500 U/kg dm), #17 (5423 U/kg dm), #18 (5212 U/kg dm), and #14 (5085 U/kg dm) (Figure 2E). This finding is in line with the limit dextrinase activities previously reported [19,22] for rice malt (3763–6940 U/kg). In barley, limit dextrinase loses its activity above 63 °C [40]. Therefore, brewers seeking to exploit the increased limit dextrinase in the rice malts will need to implement mash rests with lower temperatures to potentially enhance the debranching of starch molecules which are more readily available for β-amylase and α-amylase cleavage at higher temperatures [30].

Amyloglucosidase (AMG) and α-glucosidase may also play a role in saccharification, and their combined activity was considered using a Megazyme AMG kit [28], which does not distinguish between the two enzymes. AMG hydrolyzes starch-releasing glucose molecules and high AMG activity can increase fermentability by up to 20% [43]. α-glucosidase has been shown to convert short oligosaccharides (e.g., maltose, maltotriose, maltotetraose) in malted barley released from limit dextrinase and amylases into glucose [30]. Barley α-glucosidase is denatured during the malt kilning process [30] and has not been thoroughly studied in brewing. AMG, on the other hand, is commonly added to brew beers with a lower body or a low carbohydrate content [44]. The activity of the enzymes was measured together and ranged from 1790 to 4069 U/kg dm, with the highest AMG and α-glucosidase activities being found in #12 (4069 U/kg dm), #11 (3777 U/kg dm), #2 (3696 U/kg dm), and #5 (3583 U/kg dm) (Figure 2D).

Overall, considering the differences regarding enzymatic activity between malted barley and malted rice, future studies should focus on the differences in sugar profiles produced at different mash temperatures and compositions.

### 3.2.2. Starch Qualities

The apparent amylose content was measured in dehusked paddy rice (i.e., brown rice) and in dehusked malted rice. The apparent amylose contents of malted rice were significantly correlated ($p < 0.0001$, Pearson's correlation, Table 2) with the apparent amylose contents in paddy rice. Overall, malting increased apparent amylose content by ~2% across all samples (Figure 3A, Supplementary Materials—correlation data).

Interestingly, the average onset gelatinization temperatures (Figure 3B) of the malted rice samples were slightly higher (~1 °C) than measured in the raw rice for most cultivars, except for cultivars #2, #3, #6, #7, and #19_1—in which the malted rice had slightly lower gelatinization temperatures (~−0.4 °C)—as well as cultivar #8, wherein the raw rice and the malted rice had similar gelatinization temperatures. Peak gelatinization temperatures (Figure 3C) increased (~0.95 °C) for all but two of the rice samples (#3 and #6) after malting. The average end gelatinization temperatures (Figure 3D) increased (~1.77 °C) post-malting for all cultivars but #3, #13, #14, and #17, for which the end gelatinization temperature also decreased (~1.29 °C).

Contreras-Jiménez, Del Real, Millan-Malo, Gaytán-Martínez, Morales-Sánchez, and Rodríguez-García [45] investigated the physiochemical changes of barley starch during malting and similarly found that the gelatinization temperature of the barley starch increased as a function of malting time, which was related to the consumption of amorphous areas in the starch during the early stages of malting as well as the increases in the starch's crystallinity. Additionally, similar to the findings reported by Langenaeken, De Schepper, De Schutter, and Courtin [15], the presence of smaller starch granules could lead to an increase in the observed gelatinization temperature as the malting process progresses. Future studies should investigate if these same phenomena are responsible for the higher gelatinization temperatures observed in rice malts. Moreover, it is worth noting that onset, peak, and end gelatinization temperatures were significantly positively correlated with α- and β-amylase activities and negatively correlated with limit dextrinase activity ($p < 0.05$, Pearson's correlation, Table 2).

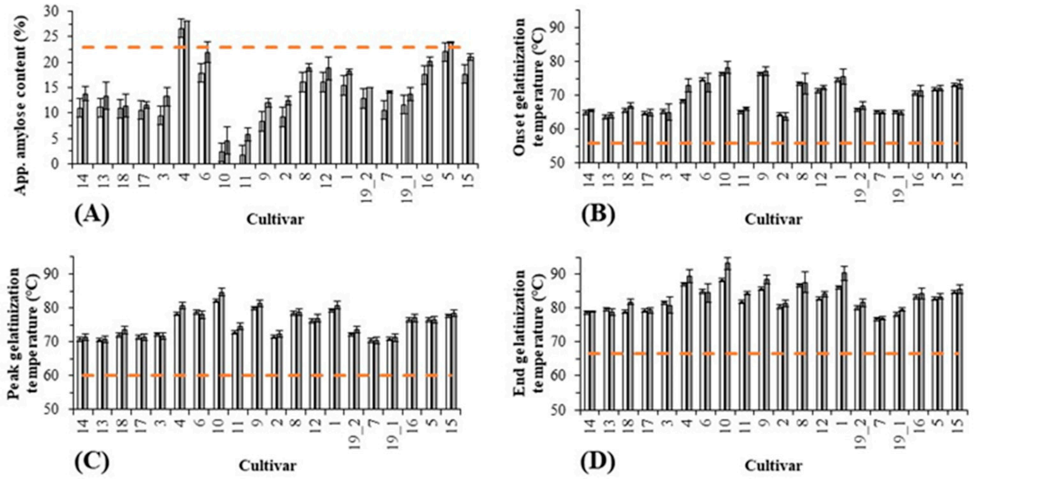


**Figure 3.** Starch characteristics of paddy rice and malted rice. (**A**) Apparent amylose content, (**B**) gelatinization temperature onset, (**C**) peak gelatinization temperature, and (**D**) end gelatinization temperature for paddy rice (white bars) and malted rice (gray bars). Samples are sorted by length/width ratio. Dashed lines show raw barley apparent amylose content (**A**) and gelatinization temperatures for barley malt (**B**–**D**) [15,46]. Data points refer to mean values ($n$ = 2), and error bars represent r, the 95% repeatability coefficient.

To investigate the impact of enzymes on the gelatinization temperature, a series of trials were performed using the DSC at different simulated mash temperatures (Table 4). The simulated mash rests were performed for 30 min at 40 °C, 45 °C, 50 °C, 55 °C, 60 °C, and 65 °C, as well as both 55 °C and 65 °C, to optimize the activities of AMG (~40 °C) [44], limit dextrinase (~50–55 °C) [47], and β-amylase (~63 °C) [48]. Cultivar #10 was chosen for this trial as it had the highest gelatinization temperature as well as high β-amylase and relatively low limit dextrinase activities. Cultivar #19_2 was also selected because it had high limit dextrinase and relatively low β-amylase activities.

**Table 4.** Impact of different temperature rests on onset, peak, and end gelatinization temperatures for malted rice cultivars #10 and #19_2.

| Cultivar | #10 | | | #19_2 | | |
|---|---|---|---|---|---|---|
| **Treatment** | **To (°C)** | **Tp (°C)** | **Te (°C)** | **To (°C)** | **Tp (°C)** | **Te (°C)** |
| Rest at 40 °C for 30 min | 78.47 | 85.36 | 93.61 | 66.82 | 74.00 | 82.73 |
| Rest at 45 °C for 30 min | 78.40 | 85.53 | 94.24 | 67.00 | 74.33 | 82.91 |
| Rest at 50 °C for 30 min | 78.74 | 85.79 | 94.05 | 67.19 | 74.65 | 84.84 |
| Rest at 55 °C for 30 min | 78.79 | 85.79 | 93.20 | 67.25 | 74.73 | 84.60 |
| Rest at 60 °C for 30 min | 79.94 | 87.13 | 94.48 | 70.61 | 75.98 | 83.79 |
| Rest at 65 °C for 30 min | 80.82 | 86.81 | 93.30 | 75.95 | 79.07 | 83.38 |
| Rest at 55 °C for 30 min + 65 °C for 30 min | 80.61 | 86.46 | 93.79 | 75.42 | 78.86 | 84.46 |

Measurements were performed only once on ground malted rice. To—onset gelatinization temperature, Tp—peak gelatinization temperature, Te—end gelatinization temperature.

Generally, increasing the simulated mash rest temperature raised the observed gelatinization onset and gelatinization peak temperatures. This suggests that limit dextrinase and amyloglucosidase (AMG)/α-glucosidase are influential in starch hydrolysis. Furthermore, if longer lower rests are applied, potentially both amorphous and crystalline structures of starch could be hydrolyzed below gelatinization temperatures. This is particularly true for cultivar #19_2, which had a high limit dextrinase activity that resulted in the onset gelatinization temperature reducing by ~9 °C after implementing a 30 min rest at 40 °C when compared to mashed in at 65 °C. Yet, further work needs to be performed to confirm this finding and should measure the hydrolysis rate of the starch via high pressure liquid chromatography (HPLC). However, this is crucial information to consider as future trials are designed to optimize the mashing profiles of specific cultivars.

#### 3.2.3. Congress Wort Viscosity

Another important finding was that the viscosity of the fine grist congress worts made with the rice malts had lower viscosities (1.36–1.71 cP, Figure 4C) than previously reported [49,50] (3.4–35.0 cP) in other malted cereals (such as black barley, spring barley, oat, wheat, rye, and corn). Unsurprisingly, wort viscosity was significantly correlated with the filtration behavior expressed as the elapsed time for the fine congress wort to pass the filter ($p < 0.01$, Table 5). This highlights the negative impact that wort viscosity has on wort filtration. Typically, <1.56 cP [38] is a rough target when breeding malted barley, and β-glucan polymers are usually some of the main components responsible for poor barley malt wort filterability [50].

On average, the wort viscosity from the different rice malts was ~1.45 cP, and all but #15 were <1.56 cP. Overall, most of these rice malts should be suitable for brewing and there should be minimal issues with regard to wort filtration. However, due to the elapsed time of the fine wort congress, some of the rice malts (#'s 2, 3, 4, 11, 13, 14, 15, 18, and 19_2) showed poor filtration behavior (>60 min, MEBAK) [24]. As previously mentioned, β-glucan was not detected in the rice, so other polymers (ex. non-saccharified starch) are likely responsible for the increases in wort viscosity and the elapsed time of the fine wort congresses observed amongst the different rice malts. However, no relationships were evident with the factors evaluated in this study (e.g., protein, apparent amylose content; see Table 5 and Supplementary Materials— Pearson 's correlation data). Future trials need to be performed on a commercial/pilot system to ensure that effective wort filtration can be achieved.

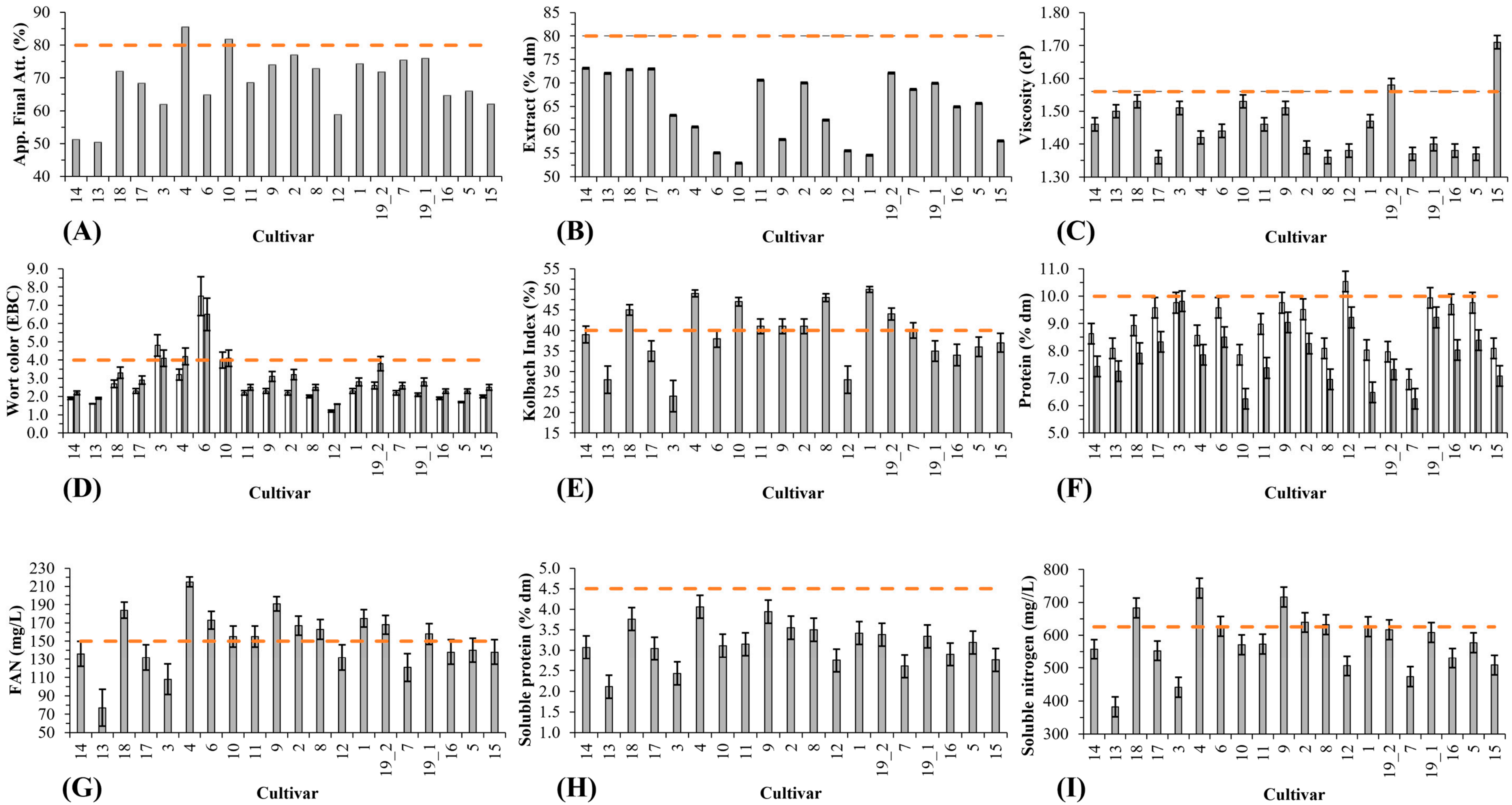


**Figure 4.** Physicochemical attributes of malted rice. (**A**) Apparent final attenuation; (**B**) fine extract of congress wort; (**C**) viscosity; (**D**) wort color (white bar) and boiled wort color (gray bar); (**E**) Kolbach index; (**F**) protein; (**G**) free amino nitrogen (FAN); (**H**) soluble protein; and (**I**) soluble nitrogen. Samples are sorted by length/width ratio. Dashed lines are values for barley malt [38,51]. Data points refer to mean values ($n$ = 2), and error bars represent r, the 95% repeatability coefficient.

**Table 5.** Pearson's correlations for congress wort qualities with paddy and malted rice attributes. Complete table with all correlations is in Supplementary Materials—Pearson's correlation tests. Main attributes in paddy rice (gray), malted rice (blue), and congress wort (yellow) are highlighted.

| Variables | Whole Kernel Length/Width | Whole Kernel Chalky Percentage | TKW (db) | Paddy Rice Protein | GE 3rd Day | GE 5th Day | Water Sensitivity | Paddy Rice Apparent AmyloseContent | Rice Onset Gel. Temp. | Rice End Gel. Temp. | Malting Losses | Rice Malt Protein | Diastatic Power | Alpha-Amylase | Beta-Amylase | Amyloglucosidase | Limit Dextrinase | Rice Malt Apparent Amylose Content | Rice Malt Onset Gel. Temp. | Rice Malt End Gel. Temp. | Viscosity | Elapsed Time of Wort | Fine Extract | Saccharification time | Apparent Final Attenuation | Soluble Nitrogen (mg/L) | Soluble Protein (%) | FAN (mg/L) | Kolbach Index | Wort Color |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Viscosity | −0.076 | 0.025 | −0.103 | −0.333 | −0.097 | −0.078 | 0.393 | −0.175 | 0.150 | 0.163 | 0.236 | −0.206 | −0.082 | −0.084 | −0.138 | −0.316 | −0.073 | −0.164 | 0.173 | 0.198 | **1** | **0.664** | −0.164 | −0.110 | −0.137 | −0.068 | −0.086 | 0.018 | 0.064 | 0.134 |
| Elapsed Time of Wort | −0.254 | 0.291 | −0.010 | −0.180 | −0.194 | −0.090 | 0.112 | −0.242 | **−0.446** | −0.217 | 0.062 | −0.012 | −0.323 | −0.334 | −0.338 | −0.114 | 0.392 | −0.241 | −0.389 | −0.162 | **0.664** | **1** | 0.341 | −0.240 | −0.048 | 0.008 | 0.008 | 0.060 | 0.026 | 0.065 |
| Fine Extract | −0.424 | 0.123 | 0.336 | −0.040 | −0.346 | −0.407 | −0.202 | −0.244 | **−0.882** | **−0.843** | −0.289 | 0.028 | **−0.628** | **−0.640** | **−0.649** | 0.079 | **0.555** | −0.306 | **−0.878** | **−0.790** | −0.164 | 0.341 | **1** | −0.381 | −0.218 | −0.158 | −0.136 | −0.274 | −0.166 | −0.369 |
| Saccharification time | 0.076 | 0.168 | −0.306 | −0.130 | −0.111 | −0.041 | 0.076 | 0.097 | 0.314 | 0.426 | −0.136 | −0.209 | 0.107 | 0.156 | 0.152 | 0.090 | −0.311 | 0.181 | 0.296 | 0.268 | −0.110 | −0.240 | −0.381 | **1** | −0.208 | −0.279 | −0.281 | −0.245 | −0.086 | 0.058 |
| Photometric Iodine Method | **−0.484** | 0.021 | 0.043 | 0.211 | **−0.635** | **−0.762** | 0.308 | −0.029 | **−0.459** | −0.405 | **−0.523** | 0.242 | **−0.550** | **−0.462** | **−0.531** | **0.444** | 0.094 | −0.074 | **−0.463** | **−0.463** | −0.192 | −0.085 | **0.483** | −0.058 | **−0.522** | −0.372 | −0.358 | **−0.511** | **−0.494** | −0.404 |
| Apparent Final Attenuation | 0.427 | 0.024 | −0.032 | −0.195 | **0.638** | **0.648** | −0.140 | −0.002 | 0.215 | 0.331 | 0.310 | −0.188 | **0.534** | **0.495** | 0.419 | −0.115 | 0.008 | −0.030 | 0.300 | **0.477** | −0.137 | −0.048 | −0.218 | −0.208 | **1** | **0.672** | **0.672** | **0.716** | **0.699** | 0.135 |
| Soluble Nitrogen (mg/L) | 0.159 | 0.015 | 0.069 | 0.117 | **0.511** | 0.434 | −0.181 | 0.219 | 0.313 | 0.376 | **0.469** | 0.061 | **0.522** | **0.608** | 0.363 | 0.116 | 0.282 | 0.189 | 0.396 | **0.489** | −0.068 | 0.008 | −0.158 | −0.279 | **0.672** | **1** | **0.999** | **0.975** | **0.739** | 0.146 |
| Soluble Nitrogen (mg/100 g dm) | 0.153 | 0.013 | 0.079 | 0.120 | **0.503** | 0.427 | −0.187 | 0.211 | 0.296 | 0.359 | **0.454** | 0.067 | **0.514** | **0.597** | 0.353 | 0.126 | 0.300 | 0.182 | 0.376 | **0.470** | −0.086 | 0.008 | −0.136 | −0.281 | **0.672** | **0.999** | **1.000** | **0.969** | **0.736** | 0.138 |
| Soluble Protein (% dm) | 0.153 | 0.013 | 0.079 | 0.120 | **0.503** | 0.427 | −0.187 | 0.211 | 0.296 | 0.359 | **0.454** | 0.067 | **0.514** | **0.597** | 0.353 | 0.126 | 0.300 | 0.182 | 0.376 | **0.470** | −0.086 | 0.008 | −0.136 | −0.281 | **0.672** | **0.999** | **1** | **0.969** | **0.736** | 0.138 |
| FAN (mg/L) | 0.236 | 0.063 | 0.014 | 0.051 | **0.581** | **0.523** | −0.193 | 0.236 | 0.366 | **0.451** | **0.544** | 0.000 | **0.591** | **0.652** | **0.449** | 0.048 | 0.190 | 0.219 | **0.461** | **0.569** | 0.018 | 0.060 | −0.274 | −0.245 | **0.716** | **0.975** | **0.969** | **1** | **0.766** | 0.215 |
| Kolbach Index | 0.142 | 0.192 | 0.236 | **−0.521** | **0.576** | **0.470** | −0.416 | 0.051 | 0.328 | 0.412 | 0.436 | **−0.610** | **0.600** | **0.538** | 0.430 | −0.081 | −0.038 | 0.023 | 0.421 | **0.569** | 0.064 | 0.026 | −0.166 | −0.086 | **0.699** | **0.739** | **0.736** | **0.766** | **1** | 0.029 |
| Wort color | −0.089 | −0.161 | **−0.600** | 0.067 | −0.056 | 0.082 | 0.105 | 0.009 | 0.240 | 0.285 | 0.100 | 0.167 | **0.502** | 0.155 | **0.697** | **−0.541** | −0.038 | 0.057 | 0.199 | 0.187 | 0.134 | 0.065 | −0.369 | 0.058 | 0.135 | 0.146 | 0.138 | 0.215 | 0.029 | **1** |
| Boiled Wort Color | −0.019 | −0.189 | **−0.542** | 0.017 | 0.088 | 0.187 | 0.115 | 0.071 | 0.223 | 0.306 | 0.187 | 0.129 | **0.554** | 0.279 | **0.695** | **−0.505** | 0.065 | 0.097 | 0.220 | 0.251 | 0.158 | 0.127 | −0.316 | −0.035 | 0.358 | 0.380 | 0.373 | 0.443 | 0.231 | **0.946** |
| pH | −0.306 | −0.173 | −0.185 | 0.384 | **−0.567** | **−0.560** | 0.247 | 0.077 | −0.174 | −0.191 | **−0.639** | 0.408 | **−0.472** | −0.352 | −0.361 | 0.280 | −0.158 | 0.071 | −0.190 | −0.330 | −0.409 | −0.380 | 0.120 | 0.314 | **−0.487** | **−0.501** | **−0.491** | **−0.603** | **−0.694** | −0.199 |

Significant ($p < 0.05$) correlations are highlighted in bold. Positive correlations are in green and negative correlations are in red. Thousand-kernel weight dry basis (TKW (db)), germination energy (GE) on 3rd day and 5th day using Aubry method, and free amino nitrogen content (FAN).

### 3.2.4. Congress Mash Saccharification

To quickly visualize whether starch was saccharified during mashing at the saccharifying rest temperature of 74 °C, an iodine solution was mixed with a sample taken from the congress mash every 5 min for 30 min (i.e., starch reacts with iodine to form blue complexes) [23]. Cultivars #18, #19_1, and #19_2 were the only rice malts to appear fully saccharified under 30 min with this test, after 15, 15, and 25 min, respectively (Supplementary Materials—correlation data). Another approach to assess the progress of saccharification is the photometric iodine method (PIM) [23,52]. Fifteen of the rice malts (#'s 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 15, 16, 18, and 19_2) had PIM values of < 0.26. In comparison, cultivars #'s 5, 14, 17, and 19_1 had values between 0.31 and 0.34, and #13 had the highest PIM value (0.69). The European Brewery Convention considers PIM values under 0.30 to be adequate regarding saccharification, but studies [53] have suggested lower thresholds (0.20–0.25).

It has been reported that malts yielding high PIM values can lead to higher turbidity, filtration problems, lower attenuation, and/or even off-flavor development. Overall, the simple iodine test and the PIM values are contradictory and indicate that the rice malts were saccharified to differing degrees. However, given the longer wort filtration times for some cultivars (such as #'s 2, 3, 4, 11, 13, 14, 15, 18, and 19_2), it is likely that complete saccharification did not occur. In addition, it is possible that if a longer rest (>30 min) and/or additional mash rests were applied than what was performed by Mayer, Marconi, Regnicoli, Perretti, and Fantozzi [21], saccharification could have reached completion.

Fine grist extract in the congress wort is obtained by converting/saccharifying the grain starch into fermentable sugars and/or dextrins. Reports in the literature [19,21,22,29,37,54] indicate a range of fine extract in malts made from rice ranging from 59.3 to 77%. The fine extracts of the rice malts measured in this study ranged from 52.9% in cultivar #10 to 73.1% in #14 (Figure 4B). Fine extract measured in the congress worts made with the rice malts was negatively correlated with gelatinization temperature and diastatic power (as well as α- and β- amylase activities) but positively correlated with width, limit dextrinase activity, and the PIM measurement ($p < 0.05$, Tables 3 and 5, and Supplementary Materials—Pearson's correlation tests). Stenholm and Home [47] also observed that limit dextrinase activity in malted barley was more limiting than α- and β- amylase activities in starch hydrolysis. This suggests that higher extract yields were related to lower gelatinization temperatures and increased limit dextrinase activity. Generally, this finding is expected [55] as starch needs to be gelatinized to be fully available for enzymatic activity. However, it also highlights the importance of limit dextrinase regarding the generation of extract in rice malt, and the entire enzymatic profile should be considered in future mashing trials.

### 3.2.5. Protein

The protein measured in the rice malts (~7.8% on average, Supplementary Materials—correlation data) was significantly positively correlated to the protein measured in the paddy rice ($p < 0.05$, Pearson's correlation, Table 2). However, total protein in the rice malts was not related to the resulting soluble protein and free amino nitrogen (FAN) measured in the congress worts ($p > 0.05$, see Tables 3 and 5, and Supplementary Materials—Pearson's correlation tests). FAN and soluble protein values measured in the congress worts made with the rice malts were higher than previously reported for rice and rice malt [19,21,22,29,37,54] and similar to the levels reported in barley malt (FAN 150 mg/L and soluble protein 4.5%) [30,38] (Figure 4G,H). This highlights that most of the rice malts potentially have enough FAN to perform healthy fermentations without the need for nitrogen supplementation. This is an interesting finding because brewers typically expect rice to have low protein content [17], and recipes such as high gravity fermentations, seltzers, and/or adjunct lagers with a high inclusion (>30%) of unmalted rice have been shown to result in stuck or sluggish fermentations and usually require some type of nutrient supplement due to low nitrogen availability [17,56]. Although not considered in this study, it is also likely that the levels of minerals measured in rice [57], such as zinc, which are also important for fermentation are equivalent to the values reported in barley [58]; however, the growing location and malting conditions could have an impact on these values. Thus, future studies should investigate the mineral content of malted rice.

Free amino nitrogen and soluble nitrogen in the fine congress wort were significantly positively correlated with the 3-day germination energy (i.e., percentage of rice kernels germinated after 3 days), diastatic power, and α-amylase activity but were negatively correlated with the pH of the fine congress wort ($p < 0.05$, Tables 2 and 5, and Supplementary Materials—Pearson's correlation tests). The relationship between germination energy and FAN is expected because cultivars with a higher germination energy would have an increased protein synthesis during germination/malting as well as an increased production of amylases [35].

The Kolbach index (KI), or the total soluble protein measured in the congress wort over the total protein measured in the malt, ranged from 24% to 50% (Figure 4E). In malted barley, the desired KI for a well-modified malt ranges from 38 to 42% [38]. Some of the rice cultivars had KI values of <38 (8 cultivars) while others had values of >42% (6 cultivars) using the current malting scheme. This indicates that the malting parameters can be further optimized in future trials as cultivars with desired malting traits are identified.

Apparent final attenuation can be used to approximate the fermentable sugars produced during mashing and is the ratio of the density at the start and end of fermentation. A higher apparent final attenuation means a higher wort fermentability, which would ultimately result in a beer with more alcohol and fewer dextrins. The mean attenuation among the rice cultivars was 69% and ranged from 50.4% and 51.2% (in #s 13 and 14, respectively) to 81.8% and 85.5% (in #10 and #4, respectively) (Figure 4A). Values reported in the literature [19,21,22,37,54,59] are between 50.0% and 86.2% for rice malts. Rice malts yielding high attenuation values and highly fermentable worts could be utilized in recipes seeking a high degree of fermentability, whereas rice cultivars yielding lower attenuation values could be interesting for producing non-alcoholic beer. Apparent final attenuation was positively correlated to grain length, germination energy, soluble nitrogen, FAN, Kolbach index, diastatic power, and α-amylase activity ($p < 0.05$, Tables 2 and 5). Stenholm and Home [47] also found, when investigating malted barley, a positive correlation for α-amylase and fermentability and no correlation for β-amylase. As aforementioned, nitrogen is important to carry out healthy fermentation [56], and diastatic power and α-amylase activity are needed for the production of fermentable sugars.

#### 3.2.6. Wort Color

Wort color pre- and post-boiling was assessed at 430 nm according to EBC 4.7 (spectrophotometric) [23] which is appropriate for barley pale malts (~4.5 EBC). Notably, the rice malts in this study were kilned based on a pale malt kilning regime. Boiled wort color from the different non-pigmented and red bran rice malts varied from very pale (1.6 EBC, #12) to pale (4.2 EBC, #4), whereas colored worts were obtained from the three purple bran rice cultivars #3, #6, and #10, and their colors were 4.1 EBC, 6.5 EBC, and 4.1 EBC, respectively (Figure 4D). The traditional measurement was not adequate for these pigmented rice malts as #3, #6, and #10 (reddish) and #4 (golden) worts had relatively similar wort color values despite their distinct visual colors (Figure 5). It has been stated [19,54] that purple-pigmented rice malts yield worts with a red-brown or pink-orange hue, due to their anthocyanin contents. Rice cultivars #3 and #6 had a wort color reduction (0.7 and 1.0 EBC) during boiling, indicating that anthocyanins may not be heat-stable. The other cultivars had a minimal color increase, 0.1–1.2 EBC, probably due to low to moderate FAN values, as wort color is commonly developed through Maillard reactions [60]. In comparison to barley, Omari, Charnock, Fugina, Thomson, and McIndoe [60] also found a lower color wort increase during boiling in worts with rice, which they speculated was due to the lower concentration of magnesium in rice.

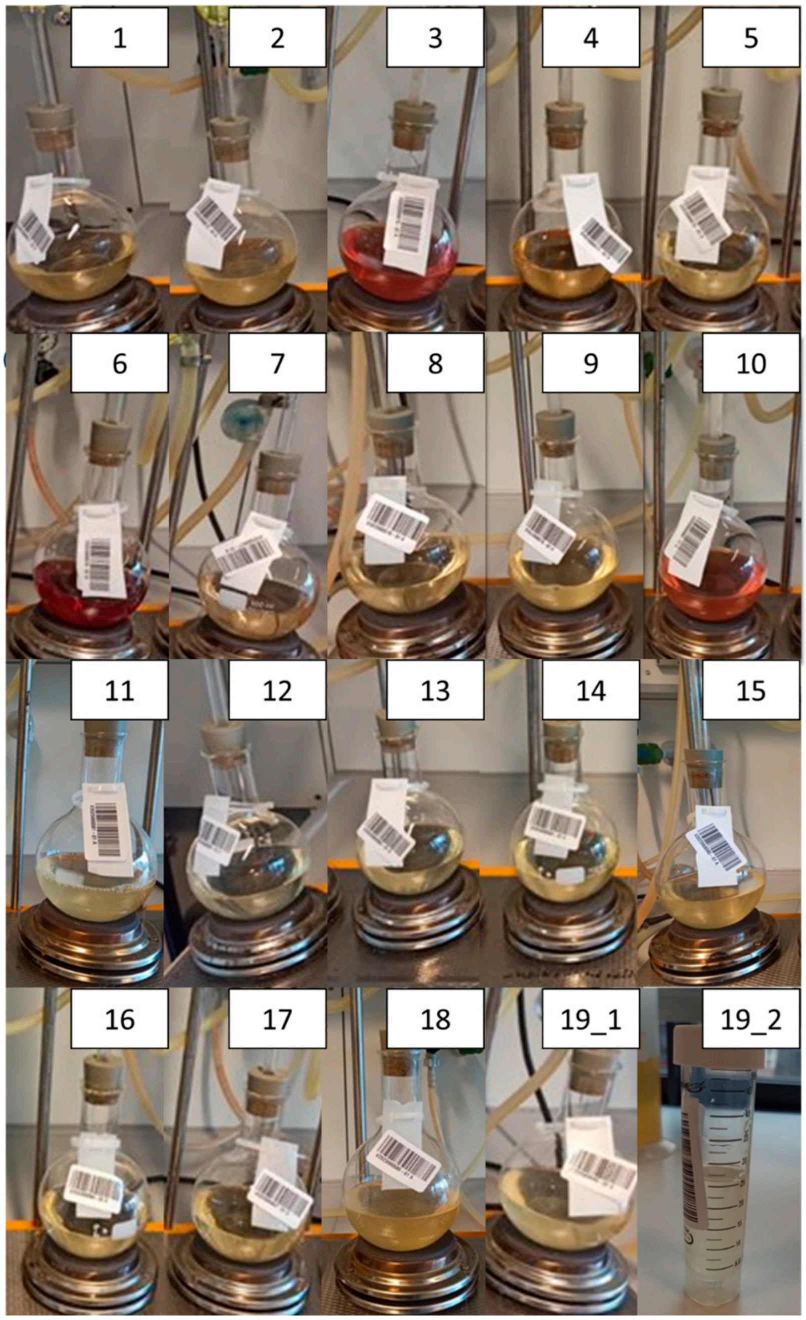


**Figure 5.** Picture of boiled worts produced with the different rice malts (cultivars #1 through #19_2). Purple-pigmented rice cultivars (#3, #6, and #10) yielded worts with a reddish color.

Specialty-colored barley malt is commonly produced during kilning, especially at higher temperatures. Recent studies [37,61–63] have shown that the inclusion of specialty-caramelized malts in recipes increases the number of aldehydes, which have a negative influence on the profile of beer and result in beers with a poor shelf life. Therefore, wort produced from malt made with purple bran opens possibilities for brewers to add color without Maillard products, which are normally associated with cardboard and caramel flavors. Future studies should investigate the stability of the color produced throughout fermentation and the flavor of beers made with these cultivars.

### 3.3. Principal Component Analysis of Paddy Rice, Malted Rice, and Congress Wort Attributes

Principal component analysis (PCA) was performed using the data from the different paddy rice, malted rice, and congress wort analyses. Principal components F1 and F2 explained 48.87% of experimental variance (Figure 6a). F3 contributed a further 10.31% (Figure 6b). Cultivars clustered on the right side are promising from a malting perspective as many properties of interest to maltsters and brewers (e.g., germination energy, α- and β-amylases, diastatic power, and attenuation) are on that side. Nevertheless, extract, a pivotal quality, is on the bottom left and near limit dextrinase, supporting the hypothesis of limit dextrinase's role in gelatinizing starch below the gelatinization temperature. Overall, long-grain rice varieties appeared to be more suitable for malting in addition to three medium grain cultivars (#4, #6, and #10), which had the longest kernels and clustered together near the long-grain rice cultivars. Short-grain rice varieties were clustered in the middle/top far-left area of the plot, displaying poorer qualities from a malting perspective (i.e., low germination energy, lower soluble nitrogen, lower final attenuation, etc.).

Cultivars #6 and #10 displayed interesting colors and malting qualities and should be further investigated. Other cultivars of interest comprise #1, #2, #3, #7, #8, #18, #19_1, and #19_2. These cultivars should be further explored in brewing trials to investigate the impact of rice malt qualities on practical brewing parameters (i.e., mashing/lautering, wort sugar profiles, etc.) and beer sensorial attributes (e.g., aroma, flavors, foam, and color).

## 4. Conclusions

By globally screening diverse rice cultivars for a wide range of physicochemical attributes, a more comprehensive understanding of how these attributes impact malted rice quality was achieved. Long-grain rice varieties seem to be more promising for malting than short and medium grains as they positively correlated with germination energy and α-amylase. Chalkiness did not significantly correlate with any malting parameter, suggesting that chalky rice may be used as a malting material without affecting its malting qualities. Fine extract was negatively correlated with gelatinization temperature, diastatic power, and α- and β-amylases, but was positively correlated with limit dextrinase. Therefore, further work should investigate the importance of limit dextrinase in relation to extract under different mashing conditions.

Purple-pigmented rice malts produced reddish wort colors, whereas red-pigmented and non-pigmented rice did not. This indicates that purple bran-derived rice malts can be used as gluten-free novel colorants, along with potentially increasing beer and beverage stability, as they contain anthocyanins and do not likely contain high amounts of Maillard products, which are normally associated with increased cardboard and caramel flavors during storage. Most cultivars had high concentrations of free amino nitrogen (FAN) and soluble proteins, disproving the idea that malted rice lacks adequate nitrogen for healthy fermentation. Additionally, rice malt made from aromatic cultivars could have the potential to bring new flavors and aromatics as viable options for brewers.

Now that rice cultivars with desired malting traits were identified, further studies should optimize malting parameters for these individual cultivars as well as analyze the practical (i.e., malt production feasibility and viability in commercial brewing processes), chemical, and sensory characteristics of beer brewed with these malted rice samples, either as an adjunct or as an all-malt product.

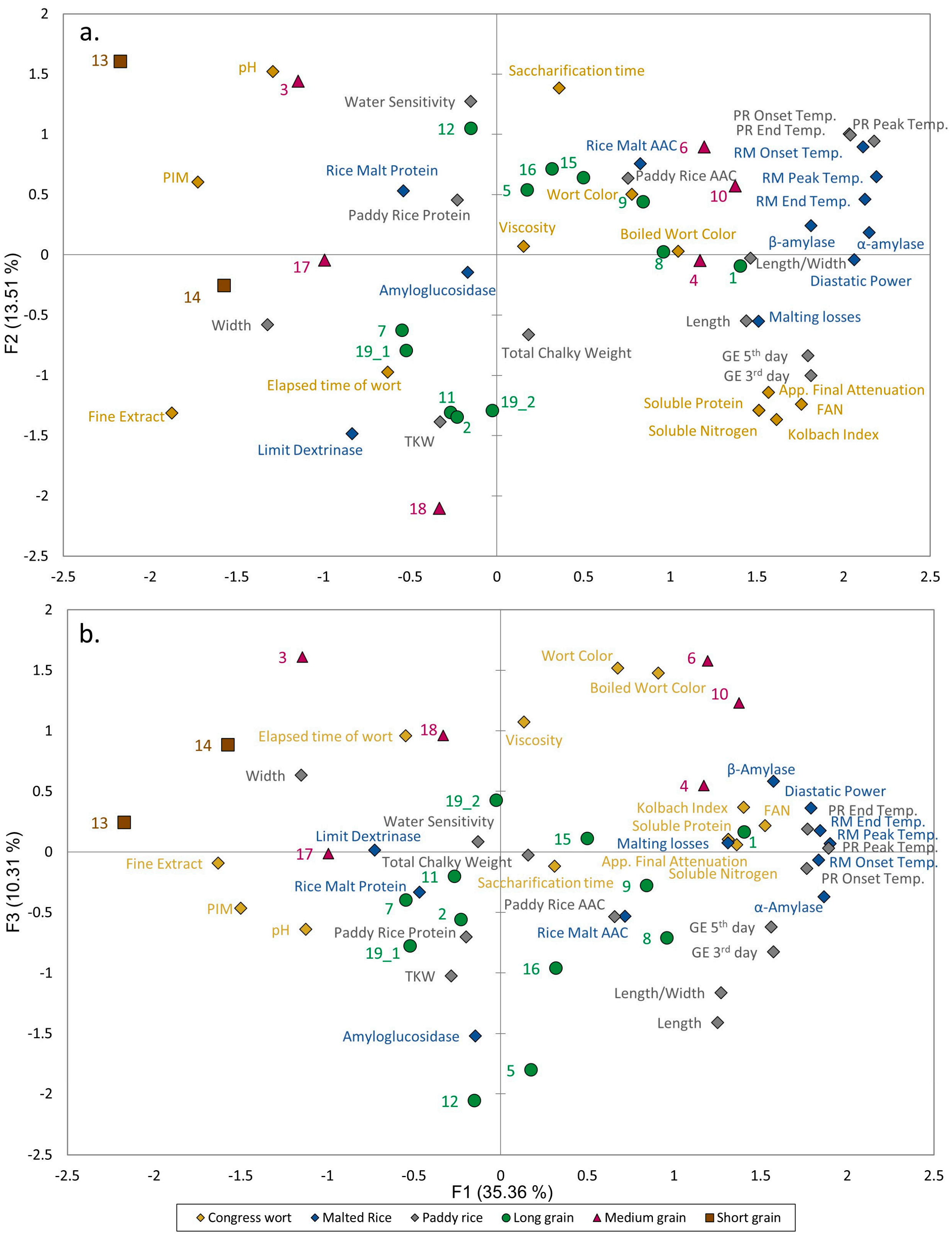


**Figure 6.** Principal component analysis biplots of paddy rice (PR) (gray diamond), malted rice (MR) (blue diamond), and congress wort attribute (yellow diamond) factors for the 20 rice samples separated into short- (brown square), medium- (pink triangle), and long- (green circle) grain rice cultivars. (**a**) F1 and F2 described 48.87% of the variation in the data, while (**b**) F1 and F3 accounted for an additional 10.31%. Photometric iodine method (PIM), apparent amylose content (AAC), germination energy using Aubry method (GE), and free amino nitrogen (FAN).

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/beverages10010016/s1. This represents all the data collected during this study, and the tabs are as follows: correlation data, Pearson's correlation tests, PCA, drying kinetics, pre-trial with 19_2, malting losses, and steeping losses.

**Author Contributions:** Conceptualization, S.L.; methodology, F.S. and S.L.; formal analysis, B.P.G. and S.L.; investigation, B.P.G., F.S. and N.R.; resources, A.M.M., S.R.M.P., G.G.A., X.S. and C.d.G.; writing—original draft preparation, B.P.G., F.S. and K.L.; writing—review and editing, F.S., N.R., S.R.M.P., G.G.A., A.M.M., X.S., C.d.G. and S.L.; visualization, B.P.G., F.S. and S.L.; supervision, S.L.; project administration, N.R. and S.L.; funding acquisition, S.L. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare that they received rice from Michael Fruge from Parish Rice.

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