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Impact of Specialty Malts on Wort and Beer Characteristics

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Abstract: Specialty malts are commonly used in brewing to provide flavor, aroma, and color to wort and beer. The use of specialty malts contributes to the variety of beer products; therefore, it is important to understand their effect on the characteristics of wort and beer. This study investigates the impact of various specialty malts on wort and beer properties. A control beer was prepared with 100% base malt, and four beer treatments were prepared with the addition of kilned, roasted, and caramel specialty malts. For each treatment, 20% of the base malt was substituted with the various specialty malts when preparing the wort. The fermentable sugars and free amino nitrogen (FAN) content for each wort were analyzed. Alcohol by volume (ABV), international bitterness units (IBU), diacetyl, and polyphenol content of each prepared beers were subsequently analyzed. Results showed that wort prepared with the addition of roasted and caramel malts contained a lower concentration of fermentable sugars and FAN than wort prepared with the base and kilned malts. Beers prepared with the addition of roasted and caramel malts exhibited the lowest levels of ABV, as well as the lowest levels of diacetyl. These beers also exhibited higher levels of total phenolic compounds compared to the other beer samples. No change was observed in IBU levels as a result of brewing with the different specialty malts. This study illustrates how the use of specialty malts impacts wort

Keywords: specialty malt; beer; fermentable sugars; polyphenols; Maillard reaction; free amino acids; diacetyl

and beer properties, providing useful information to aid in the production of quality beer products.

Citation: Castro, L.F.; Affonso, A.D.; Lehman, R.M. Impact of Specialty Malts on Wort and Beer Characteristics. *Fermentation* **2021**, *7*, 137. https://doi.org/10.3390/ fermentation7030137

Academic Editor: Maurizio Ciani

Received: 8 July 2021 Accepted: 26 July 2021 Published: 29 July 2021

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1. Introduction

Beer is a fermented beverage produced from water, malted barley, hops, and yeast. These ingredients, as well as the brewing process, will determine the final characteristics of the beer product [1]. The production of most commercial beers involves using Pilsner or Pale Ale malts as the base malt. Base malts provide the essential elements needed to produce beer, namely, fermentable sugars, free amino nitrogen (FAN), and basic malt flavor. In addition to base malts, brewers can use specialty malts to add flavor, aroma, and color to beer. These malts add complexity and diversity to a beer and are responsible for many of the different beer styles found in the market [2,3]. Specialty malts are produced using the same malting process as base malts but are subjected to higher kilning and roasting temperatures. The intensity of these kilning and roasting conditions is responsible for their characteristic colors and flavors. As a result of the high kilning and roasting temperatures, specialty malts lose their enzymatic activity —and are, therefore, used only in small amounts compared to the base malts, which retain their enzymatic activity [4,5].

Specialty malts include a wide variety of malt types. Often specialty malts are defined as any malt that is not a standard base malt. Depending on the production process, they are usually classified into three groups: Color malts, caramel malts, and roasted malts [6]. Color malts, also known as high-dried malts, display a more developed color acquired by curing at higher temperatures. The malt exposed to higher temperatures during the final stages of kilning will have a darker color and more malty/biscuit flavor than

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normally processed malts [2,6]. Caramel malts are made from fully modified, but unkilned green malt taken directly from the germination bed. The wet grains are heated to enzyme conversion temperatures, and as a result, the grains go through mashing, while still in the husk. As the heat is further increased, color and flavor compounds are developed. These malts are characterized by pleasant caramel, sweet, and sugar flavors [2,5]. Roasted malts are subjected to higher temperatures than color and caramel malts, and depending on the final product desired, green malt, finished malt, or un-malted grains can be used. Roasted malts exhibit flavors and colors which can only be developed at high temperatures, such as chocolate or coffee, but the process can also be modified to develop color with minimal flavor [2,6,7].

The color and flavor compounds produced during thermal treatment of specialty malts result from non-enzymatic browning reactions, also known as the Maillard reaction. During the Maillard reaction, reducing sugars react with amino acids and amino groups of peptides or proteins, producing malt flavor and color compounds [7,8]. Based on the nature and quantity of these compounds, they may impart different color hues and flavors to a beer, and will, therefore, affect the specific characteristics of the final beer product. For example, high-dried and caramel malts are characterized by light brown low molecular weight colorants, and the flavor is largely a result of oxygen heterocyclic Maillard reaction products, such as pyrenes, furans, and furanones. Roasted malts are characterized by intense brown high molecular weight colorants, and their flavor is mostly the result of nitrogen-containing heterocycles, such as pyrazines, pyridines, and pyrroles [7,8,9].

The Maillard reactions which occur during the production of specialty malts result in lower levels of fermentable sugars and amino acids in the wort. Previous studies have found that the lower levels of yeast nutrients in some worts will impact fermentation rate, as well as the formation of important flavor active compounds [10]. In addition, it has been reported that thermal processing can also induce a change in the polyphenol content of the specialty malt, and therefore, the wort [4,8]. The chemical composition of wort will affect the final beer quality; therefore, it is important to understand the effect of using various specialty malts on wort composition and beer quality. The objective of this study was to assess the impact of specialty malts on wort and beer chemical properties.

2. Materials and Methods

2.1. Chemicals

Sodium Carbonate (\geq 99.0%), gallic acid (\geq 97.5%), 2,3-butanedione (diacetyl, \geq 97%), and Folin–Ciocalteu reagent were purchased from Sigma-Aldrich (St. Louis, MO, USA). Reagent kits for CDR BeerLab analysis of fermentable sugars, free amino nitrogen (FAN), and IBU levels were purchased from Quartz Analytics (Rochester Hills, MI, USA).

2.2. Beer Samples

Beer was brewed using the ANVIL FoundryTM 6.5 Gallon All-In-One Electric Brewing System (Anvil Brewing Equipment, Lafayette, IN) at the California Polytechnic State University Food Science Pilot Plant. The control beer used 2-row Malt (Great Western Malting Co., Vancouver, WA) as the base malt. To brew the beers, 2.27 Kg of 2-row malt were added to 11 L of water in the electric brewing system. For each treatment beer, 20% on a weight basis of the base malt was substituted for Vienna, Munich, Crystal 60L, and Victory malts (Bries Malt and Ingredients Co., Chilton, WI). Mashing was carried out at 68 °C for one hour, the wort was recirculated during the mashing, and was separated by lautering. Sparging was performed by adding 3.79 L of water at 80 °C to the spent grains. The wort was brought to a boil, Fuggle hops (28.35g) were added, and the wort was boiled for 60 minutes. After the boiling process, the wort was recirculated until it obtained a clear appearance; it was then cooled and transferred into a 3.5 gallon conical fermenter (Ss Brewtech, Tustin, CA), where it was fermented with an ale yeast (CALI premium beer yeast, Cellar Science). Original gravity for wort prepared with Control, Munich, and

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Vienna malts was 13.71°P, while original gravity for wort prepared with Victory and Crystal malts was 12.92°P and 12.80°P, respectively. Fermentation was performed at 21 °C until final gravity readings were constant (approximately 14 days). Fermentations were carried out in triplicate, and the final volume of the beers was 9.46 L per replicate.

2.3. Sample Preparation

Beer samples for analysis were tempered at 20 °C and degassed using an ultrasonic bath for 10 minutes. Wort samples for analysis were tempered at 20 °C.

2.4. Determination of Wort Fermentable Sugars

The fermentable sugar content of wort samples was measured using a CDR BeerLab Analyzer, fermentable sugar pre-filled reagent kits were utilized for the analysis (Quartz Analytics, Rochester Hills, MI, USA).

2.5. Determination of Wort Free Amino Nitrogen (FAN)

FAN of wort samples was measured using a CDR BeerLab Analyzer, FAN pre-filled reagent kits were utilized for the analysis (Quartz Analytics, Rochester Hills, MI, USA).

2.6. Determination of Wort Gravity and Beer Alcohol Content

An Anton Paar Density Meter 4500M and Alcolyzer (Anton Paar, Graz, Austria) was used to measure the wort specific gravity and beer alcohol content (% v/v) of degassed beer samples using the ASBC Method of Analysis Beer 4G [11].

2.7. Determination of Beer Bitterness

Bitterness was measured using a CDR BeerLab Analyzer, bitterness pre-filled reagent kits were utilized for the analysis (Quartz Analytics, Rochester Hills, MI, USA).

2.8. Determination of Beer Diacetyl Content

Diacetyl was determined using the ASBC Method of Analysis Beer-25F [12]. Quantification of the volatile compounds was performed using an Agilent 7890B gas chromatograph with a flame ionization detector (GC/FID, Agilent Scientific, Santa Clara, CA).

2.9. Determination of Total Polyphenols in Beers

The total polyphenol content of the beer samples was determined using the Folin–Ciocalteu method [13]. A gallic acid stock solution was prepared by dissolving 0.500g of gallic acid in 10 mL of ethanol and diluting it to 100 mL in a volumetric flask; the stock solution was used to prepare a calibration curve in the range of 0–500 mg gallic acid/L. For the analysis, 20 μL of blank, beer sample, and gallic acid calibration solution were placed in separate cuvettes, to each cuvette, a volume of 1.58 mL of water and 100 μL of the Folin–Ciocalteu reagent was added and allowed to sit for 8 minutes, then 300 μL of a 20% sodium carbonate solution were added. The mixture was allowed to react for 2 hours, then the absorbance of the prepared samples was measured at 765 nm using a UV-1900i spectrophotometer (Shimadzu, Columbia, MD, US). The total polyphenol content was quantified from the gallic acid standard curve, and results are expressed as gallic acid equivalents (GAE) in mg/L.

2.10. Data Analysis

Data analysis was performed utilizing JMP Statistical software (version 15.1; Cary, NC). One-way analysis of variance (ANOVA) was performed on measured parameters with a statistical significance set at $p \le 0.05$. Tukey's honest significant difference (HSD) mean separation was used to determine significant differences. All analyses were performed in triplicate.

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3. Results and Discussion

3.1. Chemical Composition of the Worts

Analysis of fermentable sugars and free amino nitrogen (FAN) was performed on worts prepared with the substitution of 20% of the base malt (2-row malt) with various specialty malts (Munich, Vienna, Crystal, Victory). A control wort was prepared with 100% 2-row malt. Results for the analysis are shown in Table 1. Statistical analysis showed that fermentable sugar content in samples prepared with Victory and Crystal malts was significantly lower ($p \le 0.05$) compared to the other samples and the control. There was no significant difference ($p \le 0.05$) between the fermentable sugar content of the control and the samples prepared with Munich and Vienna malts. The data for FAN showed a significant difference ($p \le 0.05$) between the control and all other samples, but no significant difference between the samples prepared with the addition of Munich and Vienna malts. FAN levels were lower in worts prepared with specialty malts, with the lowest values observed in the samples prepared with the Victory and Crystal malts. Results indicate that the substitution of 20% of the base malt with specialty malts impacts the fermentable sugars and FAN content of the wort.

Table 1. Properties of wort prepared with 20% specialty malt substitutions.

Malt Type	Level of Malt (%)	Fermentable Sugars: Glucose + Fructose + Maltose (g/L)	Free Amino Nitrogen (mg/L)
2-Row (Control)	100	$98.70^{a} \pm 0.10$	255.33° ± 1.73
Munich	20	$96.33^{a} \pm 0.25$	$234.33^{b} \pm 2.89$
Vienna	20	$96.83^{a} \pm 0.06$	$230.10^{b} \pm 3.61$
Crystal	20	$81.67^{\rm b} \pm 0.29$	$200.67^{\circ} \pm 8.50$
Victory	20	$84.63^{\circ} \pm 0.06$	$219.67^{d} \pm 2.08$

Values are expressed as mean of 3 replications (n = 3) \pm standard deviations. Different letters in the same column indicate significant differences as analyzed by Tukey's HSD ($p \le 0.05$).

During the production of malts, amylase enzymes are produced, which are important for breaking starch down into fermentable sugars during the mashing process. The ability of the malt enzymes to break down starches into fermentable sugars is referred to as the enzymatic power of the malt, base malts, such as the 2-row malt used for the control in this study, have high enzymatic power, and are, therefore, used to provide the fermentable sugars in the wort that the yeast will utilize during fermentation [7,14,15]. The fermentable sugar content of worts prepared with the addition of Munich and Vienna malts was not significantly different ($p \le 0.05$) from that of the control wort. Munich and Vienna malts are categorized as kilned malts—during processing, they are kilned at relatively low temperatures for several hours, and as a result, they retain all or most of their enzymatic power [7]. It is very likely that due to the high enzymatic power of both Munich and Vienna malts, the worts produced with the addition of these malts resulted in similar levels of fermentable sugars as the control.

The worts prepared with the addition of Crystal and Victory malts contained significantly lower levels of fermentable sugars ($p \le 0.05$) compared to the control. Crystal and Victory malts are classified as caramel and roasted malts, respectively. These malts are subjected to higher temperatures than kilned malts to develop a broad range of colors and flavors, and because of the high temperature processing, they lose their enzymatic power, and therefore, must be accompanied by a base malt during brewing [7,14,15]. The loss of enzymatic power during the processing of the Crystal and Victory malts explains why the substitution of 20% of the base malt with these specialty malts resulted in worts with lower levels of fermentable sugars compared to the control.

The data in Table 1 shows that the substitution of the base malt with 20% of the different specialty malts resulted in worts with lower levels of FAN. These results suggest that the Munich, Vienna, Victory, and Crystal malts had lower levels of FAN compared

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to the base malt, and therefore, produced worts with lower levels of FAN. About 70% of the wort FAN is produced during malting, and it is derived from the breakdown of the endosperm proteins by proteolytic enzymes. Therefore, malts that are high in nitrogen content produce worts that are rich in FAN [16,17]. During the processing of malts, nonenzymatic browning reactions occur between amino acids and reducing sugars; the reaction generates both color and flavor compounds. Specialty malts are usually kilned or roasted at higher temperatures than base malts, which results in higher amounts of color and flavor compound production, as well as higher consumption of amino acids during the non-enzymatic browning reactions [10,16]. It is very likely that the specialty malts used in this study contained lower levels of FAN compared to the base malts because of the higher temperatures used during their production, which resulted in an increased consumption of the amino acids. These results agree with a previous study by Coghe et al. (2005), where the researchers observed that using darker specialty malts resulted in a reduction in FAN [10].

3.2. Chemical Composition of the Beers

In addition to their effect on wort composition, the impact of specialty malts on final beer properties was also evaluated. Analysis of alcohol by volume (ABV), International Bitterness Units (IBU), total polyphenols, and diacetyl content was performed on beers prepared from the fermentation of the worts formulated with the control and specialty malts. Results for the analysis are shown in Table 2. A decrease in ABV was observed when specialty malts were utilized, ABV was significantly lower ($p \le 0.05$) for beers brewed with the addition of Victory and Crystal malts compared to the other beer samples and the control. No significant difference ($p \le 0.05$) was observed between the ABV of the control and the beer samples prepared with Munich and Vienna malts. These results can be explained based on the wort composition analysis. As previously discussed, worts prepared with the addition of Victory and Crystal malts contained the lowest amounts of fermentable sugars (Table 1); therefore, it is expected that beers prepared from the fermentation of these worts would produce beers with lower ABV compared to the other beer samples. The lower ABV in beers brewed with Crystal and Victory malts could also be attributed to a higher presence of Maillard reaction products compared to the other samples. Previous research has demonstrated that certain Maillard reaction products have inhibitory effects on yeast metabolism [10,18], therefore it is possible that the higher presence of these compounds in the Crystal and Victory malts had a detrimental effect on yeast metabolism, leading to the lower ABV observed. The impact of specialty malts on ABV is of interest to brewers as the ABV is a critical quality indicator in beer—it indicates the strength of the beer and impacts the flavor, body, and mouthfeel [1].

Table 2. Properties of beers prepared with 20% specialty malt substitutions.

Malt Type	Level of Malt (%)	ABV (% v/v)	Polyphenols (mg GAE/L)	IBU
2-Row (Control)	100	$6.51^a \pm 0.02$	$91.65^{a} \pm 0.12$	$19.33^a \pm 0.76$
Munich	20	$6.52^a \pm 0.01$	$75.34^{b} \pm 1.21$	$18.80^{a} \pm 0.66$
Vienna	20	$6.48^{a} \pm 0.01$	$93.50^{a} \pm 5.15$	$20.27^a \pm 1.01$
Crystal	20	$5.92^{b} \pm 0.01$	$113.67^{\circ} \pm 5.78$	$19.80^{a} \pm 1.78$
Victory	20	$6.13^{b} \pm 0.01$	$116.27^{\circ} \pm 3.10$	$19.33^a \pm 1.59$

Values are expressed as mean of 3 replications (n = 3) \pm standard deviations. Different letters in the same column indicate significant differences as analyzed by Tukey's HSD ($p \le 0.05$).

Bitterness is another quality indicator of extreme importance to brewers, as it impacts a beer product's acceptance by consumers, it is normally measured utilizing the IBU scale. Results show that the addition of specialty malts did not influence the final beer IBU levels. As can be seen in Table 2, the IBU level values ranged from 18.80 ± 0.66 to 20.27 ± 1.01 , with no significant difference between the values ($p \le 0.05$). It is important to emphasize that the IBU scale is an analytical tool that measures the content of iso- α -acids in the beer

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sample, and while it is useful to brewers to describe bitterness with some level of consistency, the IBU value does not necessarily describe the perceived bitterness level of a beer. Previous research has shown that melanoidins and pyrolysis products in dark specialty malts can impart bitterness to a beer [19]; therefore, a sensory test would be necessary to completely determine if a change in the bitterness perception results from the addition of 20% of the specialty malts used in this study.

Another parameter that has an important impact on beer quality is the polyphenol content. Polyphenols in beer have been associated with haze formation through protein binding. Haze active polyphenols from protein-polyphenol complexes, leading to the formation of haze or turbidity in beer, a visual characteristic considered a defect by most consumers in the final product [20]. Polyphenols are also associated with flavor stability because of their antioxidative properties. Polyphenols are known as potent antioxidant compounds, and previous studies have found that polyphenols can inhibit oxidative deterioration reactions, resulting in beers with prolonged flavor stability [21]. Malt is one of the major contributors of polyphenols to beer; therefore, it is important to understand the effect of different malts on the polyphenol content of the final beer product.

The content of polyphenols in the final beers was measured utilizing the Folin–Ciocalteu method, and results are shown in Table 2. As can be seen from the results, the highest concentration of polyphenols was observed in the beers brewed with the addition of Crystal and Victory malts. The final content of phenolic compounds in beer depends on the raw materials used; Crystal and Victory malts are classified as caramel and roasted malts, respectively, and previous research has shown that these darker specialty malts contain higher concentrations of polyphenols than kilned malts [22,23], and worts produced with the addition of these specialty malts contain a higher concentration of polyphenols compared to worts produced from kilned malts [4]. Therefore, it would be expected that beers produced with the addition of caramel and roasted malts would have a higher polyphenol content—this is corroborated in our results and agrees with previous studies which have shown that the total polyphenol concentration is higher in beers produced with dark specialty malts compared to beers produced with lighter colored kilned malts [24,25].

The diacetyl content of the beer samples was determined in addition to the ABV, IBU, and polyphenol content analysis. Diacetyl is a vicinal diketone produced during fermentation as a by-product of synthesizing amino acids by Saccharomyces yeast. Diacetyl imparts a butter or butterscotch flavor to beer—it is generally considered an off flavor, therefore it is important for brewers to understand the effect of wort composition on the production of diacetyl during brewing [26,27]. Results for the analysis of diacetyl are shown in Table 3; it can be observed that beers brewed with the addition of Victory and Crystal malts showed diacetyl levels between 25 ± 3 and 28 ± 4 ppb, while beers brewed with the kilned malts (Control, Munich, Vienna) contained diacetyl levels between 49 ± 1 and 189 ± 7 ppb. According to our results, the addition of specialty malts influenced the production of diacetyl.

Table 3. Diacetyl content of beers prepared with 20% specialty malt substitutions.

Malt Type	Level of Malt (%)	Diacetyl (ppb)	
2-Row (Control)	100	49 ± 1	
Munich	20	189 ± 7	
Vienna	20	92 ± 4	
Crystal	20	28 ± 3	
Victory	20	25 ± 4	

Values are expressed as mean of 3 replications (n = 3) \pm standard deviations.

Fermentation studies have indicated that the wort content of FAN can influence the formation of vicinal diketones. During fermentation, the brewing yeasts utilize the available nitrogen present in the wort for the synthesis of new amino acids, cellular proteins,

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and cell compounds. Hence, changes in the FAN composition of the wort will impact nitrogen metabolism, and the subsequent biosynthesis of flavor active compounds like vicinal diketones [16, 28]. According to our results, worts prepared with Crystal and Victory malts contained the lowest amount of FAN (Table 2), and the beers prepared with these worts exhibited the lowest content of diacetyl (Table 3). These results are consistent with those observed by Krogerus and Gibson (2013), who reported that decreasing the FAN level in wort led to a decrease in diacetyl production during fermentation [29]. A study by Pugh et al. (1987) also reported a decrease in diacetyl concentration during fermentation as FAN content was decreased in the wort [30]. Our results strongly suggest a correlation between wort FAN level and diacetyl production.

4. Conclusions

Results from this study indicate that the substitution of 20% base malt with various specialty malts during wort production influences the properties of the wort and the beers produced from these worts. Worts prepared with the addition of caramel and roasted malts had lower levels of fermentable sugars and free amino nitrogen (FAN) compared to the other wort samples and the control. The reduction in the level of fermentable sugars and FAN is likely the result of non-enzymatic browning reactions, which are more intense in the caramel and roasted malts as they are subjected to higher temperatures than kilned malts.

The wort nutrient levels had an impact on the final beer properties. Beers produced from the fermentation of worts prepared with the addition of caramel and roasted malts were characterized by a lower ABV compared to the other beer samples, suggesting that yeast metabolism may have been affected by the lower nutrient levels, or the presence of higher concentrations of non-enzymatic browning reaction products. The IBU levels were not affected by the addition of specialty malts; however, future studies should focus on sensory testing to determine if the addition of specialty malts has an impact on the perceived bitterness. Higher phenolic content was found in beers produced with roasted and caramel malts, indicating that these darker beers could potentially provide a higher antioxidant potential, which would be beneficial to human health. Finally, our research indicates that a lower level of FAN in wort is associated with lower diacetyl production during fermentation.

This research has demonstrated that using specialty malts can impact wort composition and final beer properties. This information is important to brewers, as understanding the role of specialty malts on beer properties will help select and manipulate specialty malts to produce quality beer products. Further research is suggested to determine the effect of specialty malts on antioxidative activity in beers, as well as perform sensory characterization and aging studies.

Author Contributions: L.F.C. conceptualized the research, designed the experiments, performed analytical measurements, performed the statistical analysis, interpreted results, and wrote the manuscript. ADA assisted in the preparation of the wort and beer samples, data collection, and assisted with the writing of the manuscript. RML assisted in the brewing of the samples, data collection, and assisted with final edits of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable. **Data Availability Statement:** Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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