fermentation

MDPI

Review

The Role of Malt on Beer Flavour Stability

Luis F. Guido * and Inês M. Ferreira

LAQV/REQUIMTE, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

* Correspondence: lfguido@fc.up.pt; Tel.: +351-220-402-644

Abstract: Delaying flavour staling has been one of the greatest and most significant challenges for brewers. The choice of suitable raw materials, particularly malting barley, is the critical starting point to delay the risk of beer staling. Malting barley and the malting process can have an impact on beer instability due to the presence of pro-oxidant and antioxidant activities. Malt contains various compounds originating from barley or formed during the malting process, which can play a significant role in the fundamental processes of brewing through their antioxidant properties. This review explores the relationship between malt quality, in terms of antioxidant and pro-oxidant activities, and the flavour stability of beer.

Keywords: beer staling; malt quality; beer stability; beer flavour; antioxidant activity; pro-oxidant activity

1. Introduction

There has been controversy about the pathways involved in the synthesis of beer staling compounds. Although the filling and packaging processes and storage conditions are widely recognised as playing a central role, attention is being increasingly directed towards the properties of barley malt and the malting technique to better understand the factors affecting beer flavour stability. Malt is responsible for providing the principal colour of beer, and different malt types and malting conditions are responsible for both positive and negative flavours in beer [1]. The scarce knowledge on the significance of the balance between the antioxidant and pro-oxidant potential exhibited by barley and malt has motivated our research team to conduct studies aiming at elucidating the contribution of individual components to the overall antioxidant capacity of malt. A comprehensive review of the overall antioxidant properties of malt and how they are influenced by individual constituents of barley and the malting process may be accessed [2].

Although the staling of beer is a complex phenomenon, volatile carbonyl compounds have attracted most attention in the context of beer flavour instability. However, the myriad of flavour notes changing during staling is due to a much broader range of chemical entities. Unsaturated aldehydes, especially those with very low sensory thresholds having 7 to 10 carbon atoms, are considered to be the most important. Amongst them, *E*-2-nonenal, with an extremely low flavour threshold of 0.11 µg/L (Table 1), has long been the most frequently cited as the cause of a cardboard character typical of aged beer [3]. These aldehydes are potentially formed during malting and mashing by a number of different routes, in which the enzymatic and non-enzymatic degradation of polyunsaturated fatty acids is assumed to be the major source [4].

Acetaldehyde is the predominant carbonyl compound present in beer, making up around 60% of all aldehydes [5]. Despite this, its high flavour threshold (Table 1) means that it does not typically contribute significantly to beer flavour, except in rare cases such as when it causes a "green taste" in young beers [6]. In contrast, the most prominent aroma in a 6-month-old beer sample is often identified as *E*-β-damascenone, a terpenic ketone characterized by a "stewed apple," fruity, and honey-like note (Table 1, [7]). According

check for updates

Citation: Guido, L.F.; Ferreira, I.M. The Role of Malt on Beer Flavour Stability. *Fermentation* **2023**, *9*, 464. https://doi.org/10.3390/fermentation9050464

Academic Editors: Maria Dimopoulou, Spiros Paramithiotis, Yorgos Kotseridis and Jayanta Kumar Patra

Received: 14 April 2023
Revised: 10 May 2023
Accepted: 11 May 2023
Published: 13 May 2023

to some authors, *E*-β-damascenone may be just as significant to the flavour of aged beer as *E*-2-nonenal [8,9]. Furanic aldehydes, such as furfural and 5-hydroxymethyl furfural, are often associated with the development of caramelized stale flavours, but it is widely accepted that these compounds are not directly responsible for such flavours [10].

The Strecker degradation is a chemical reaction between an amino acid and an alpha-dicarbonyl compound, such as those that are intermediates in the Maillard reaction. This reaction converts the amino acid into an aldehyde with one less carbon atom. While the aldehydes produced through the Maillard reaction and Strecker degradation are not typically considered to be the primary beer staling compounds, recent research has shown that aldehydes resulting from the Strecker degradation, such as 2-methylpropanal, 3-methylbutanal, and phenylacetaldehyde, can be found in higher concentrations in malt compared to other types of aldehydes. 3-Methylbutanal was found in the highest concentration (1213–8218 μg kg^{-1}), followed by 2-methylpropanal (612–3469 μg kg^{-1}), and phenylacetaldehyde (198–5105 μg kg^{-1}) [11,12].

In brief, nearly all the aldehydes that are considered aging indicators in beer are already present in malt [13]. Fickert and Schieberle (1998) identified several aldehydes in the volatile fraction of barley malt, including *E*-2-nonenal, which suggests that both lipid peroxidation and the Strecker degradation are important reactions for generating flavours during malt production [14].

Table 1. Sensory descriptors and flavour threshold values of carbonyl compounds in lager beers.

Compound	Flavour Threshold (mg/L)	Sensory Descriptor
Carbonyl Compounds		
Acetaldehyde	25 [a]	Green leaves, fruity
(*E*)-2-nonenal	0.00011 [a]	Papery, cardboard
(*E*)-β-damascenone	0.15 [b]	Stewed apple, honey-like
Furfural	150 [a]	Sweet, bready, caramellic
5-Hydroxymethyl-furfural	1000 [a]	Fatty, waxy, caramellic
Diacetyl	0.1–0.2 [c]	Butterscotch, rancid
2,3-Pentanedione	1 [c]	Fruity, sweet

[a] [15]; [b] [16]; [c] [17].

2. From Barley to Malt

The barley is transformed into malt through the malting process, which is mainly the transformation of insoluble starch into simple sugars. The malting process consists of three technological steps: steeping, germination, and kilning or roasting (final heat treatments).

During the steeping stage, the raw barley is soaked in water to increase the grain's moisture content from approximately 12% up to 46%. The moisture increase induces the beginning of germination and the early growth of the embryo, resulting in the activation and development of diastatic enzymes. The starch is then released from the endosperm and converted into simple sugars. Usually, the steeping step consists in alternating periods where the grains are submersed in water with rest periods or dry periods, with a duration of 36–48 h at a temperature of 15–20 °C [18,19].

The next step consists of the germination of steeped barley to obtain "green malt". The "green malt" is characterized by high moisture contents (up to 47%) and high enzymatic activity, resulting in the hydrolysis of cell walls and starch mediated by α-amilase, β-amylase, and β-glucanases. The germination step lasts for 4–6 days and it is conducted at temperatures around 15–22 °C. The moisture of the grains is kept around 45% and the growth of the rootlets is controlled to evaluate the degree of sprouting [18,19].

After germination, the moisture content of "green malt" must be reduced (to approximately 5%) in order to stop germination and assure optimal conditions for the conservation and storage of the grains. This is achieved by submitting the grains to a final heat treatment step (kilning), which will halt the sprouting process and avoid all the starch reserves that are consumed by deactivating enzymatic activity. The kilning process consists of a first

phase called the withering phase, where the grains are exposed to temperatures between 50–65 °C for 12, reducing the moisture content to approximately 12% and halting the germination (above 40 °C). The second phase (curing phase) is carried out at temperatures up to 82–85 °C for 4 h, reducing moisture to values around 4% and ensuring enzyme inactivity. The grains are then cooled down to ensure an ideal temperature for discharge and storage [18,19].

The thermal processing steps have the greatest impact on the colour and flavour of malt. The obtained malted grains are usually called pale malt and are applied in almost all types of beer. Light malt is commonly fast-dried to limit the formation of Maillard reaction products, while for specialty dark malts the moisture is reduced slowly in order to achieve higher grain temperatures, inducing the Maillard reaction [20].

Specialty malts are produced to provide characteristic flavours and colours to beer, but they are typically used in very small amounts (<5%) compared to pale malt. They can be produced by roasting barley, green malt, or kilned pale malt [2,20]. resulting in low enzymatic activity and low levels of fermentable sugars and amino acids. Specialty malts are primarily used to add colour and aroma to beer. Specialty dark malts are generally classified into coloured malts, caramel malts, and roasted malts, which are obtained through roasting at temperatures ranging from 110 to 220 °C. Different degrees of roasting, which are determined by time and temperature, result in various intensities of colour and flavour through the Maillard and caramelization reactions, as well as pyrolysis reactions at high temperatures (>150 °C) [2,20,21].

The primary flavour characteristics of malt are developed during the malting process. However, recent studies have focused on understanding the impact of different barley varieties on the flavour of the beer. Through analysis of various barley varieties, researchers have identified how different metabolites influence the chemistry and flavour of the beer. The presence of various compounds, such as aldehydes, ketones, alcohols, furans, and aromatic compounds, contributes to the unique chemical composition of the final beer and thus, imparts its distinctive sensory attributes [22,23].

3. Malt Antioxidant Activity

Antioxidants can be broadly defined as compounds that inhibit oxidative reactions by decreasing molecular oxygen levels, scavenging chain-initiating and chain-propagating free radicals, chelating metals, or decomposing peroxides [24]. As such, they are believed to play a crucial role in malting and brewing by inhibiting oxidative damage.

Sulphites and ascorbic acid are commonly used as antioxidants during brewing to produce beers with high antioxidant activity [25]. However, due to consumer demand and stricter regulations, there has been a trend toward reducing the use of added antioxidants. Consequently, more attention is now being given to the brewing process and the properties of raw materials. Barley malt already contains various endogenous antioxidants such as phenolic compounds, phytic acid, ascorbic acid, and enzymes [26]. Protecting the endogenous antioxidants present in barley during malting can increase the brew's reduction potential, thus inhibiting oxidative processes harmful to flavour stability and avoiding the use of exogenous antioxidant compounds [27]. Important antioxidant compounds in malting and brewing include:

(i) Melanoidins and reductones

Maillard reaction products (MRPs) are formed by the reaction between carbonyl groups of reducing sugars and amino groups of amino acids, peptides, or proteins, yielding a complex mixture of compounds with different molecular weights. The polymerization of low molecular weight compounds into high molecular weight compounds, also designated as melanoidins (MLD), may occur in the late stages of the Maillard reaction. MLD (Figure 1) are important for the quality and characteristics of many types of foods and beverages not only due to their colour and aroma, but also due to their health benefits and antioxidant properties [2]. MRPs act as scavengers for reactive oxygen species such as superoxide, peroxide, and hydroxyl radicals. They are known to be highly efficient antioxidants in the

production and storage of food. MRPs have been found to have metal chelating properties, to be effective at reducing hydroperoxides to non-radical products, and to break the radical chain by donating a hydrogen atom [26]. Studies have reported that the antioxidant capacity of malt can increase during kilning and roasting as a result of the Maillard reaction, which leads to the development of reductones and MRPs [28–32]. MRPs have been identified as the primary contributors to the antioxidant activity of roasted malts [30,33], with a positive influence on the maintenance and development of malt-reducing properties [34].

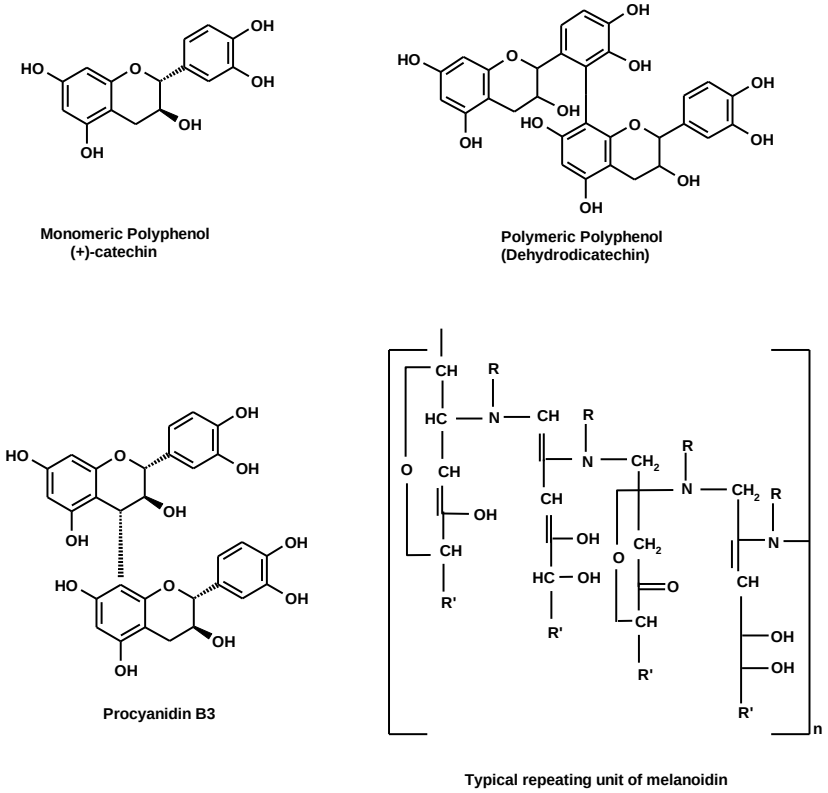

Figure 1. Chemical structures for some important antioxidant species, naturally present in barley malt.

(ii) Phenolic substances (phenolic acids and polyphenol compounds)

Barley contains 100 to 400 mg/kg of phenolic compounds, consisting of 80% of flavan-3-ols, 13% of flavonols, 5% of phenolic acids, and 2% of apolar compounds. Among flavan-3-ols, the most abundant compounds are the monomer forms, (+)-catechin and (−)-epicatechin, and polymer forms, constituted mainly by units of (+)-catechin and (+)-gallocatechin (Figure 1). Monomeric, dimeric, and trimeric flavan-3-ols accounted for 58% to 68% of the total phenolic content, with a predominance of trimeric flavan-3-ols [35].

Phenolic compounds are effective radical scavengers and can inhibit non-enzymatic lipid peroxidation. They also act as enzymatic lipid peroxidation inhibitors, as discussed below. Malt and hops both contribute these substances to wort and beer, but the majority comes from the malt. Malt-derived polyphenols account for about 70–80% of the polyphenols in the wort, with the remaining 20–30% coming from hops. The properties of the polyphenols from these two sources are likely to be different and highly dependent on the degree of polymerization. Lower molecular weight polyphenols are particularly effective as antioxidants, with the reducing power and solubility of polyphenols decreasing with increasing molecular weight.

The contribution of malt to the redox potential, and its status throughout the brewing process and in the final beer, depend on various factors and the interactions between different reducing agents. It is important to note that in certain situations, reducing agents

can become pro-oxidants. Therefore, the oxidation/reduction state plays a crucial role in the deterioration of beer, and an increase in reducing activity is beneficial for enhancing flavour stability.

The antioxidant capacity of barley is primarily attributed to its polyphenols, which can vary depending on the barley variety. Therefore, selecting the appropriate barley variety is the first step in reducing the potential for oxidation. Research has shown that most of the polyphenols found in malt are already present in barley, indicating that the natural antioxidants in barley make a significant contribution to the antioxidant activity of malt [36]. Low-molecular-weight polyphenols (<5 kDa) are responsible for 80% of the antioxidant activity in malt and beer samples [37]. The kilning stage during malt production also has a considerable impact on the antioxidant levels and reduction potential of malt. The formation of melanoidins and reductones during kilning significantly influences the concentration of MRPs in malt, and this is affected by the kilning temperature and time. The malting process, in particular the kilning regimes and roasting temperatures, may have an important impact in terms of the phenolic composition and antioxidant features. Among the malts studied, extracts from light types (kilning temperature $\leq$160 °C) contained higher amounts of total and individual phenolic compounds, ferulic and *p*-coumaric acids in particular, than dark extracts (malt kilning temperature $\geq$200 °C) [38].

Recent studies have revealed that phenolic compounds can inhibit lipoxygenases from germinating barley [39]. The effectiveness of phenolic compounds in inhibiting autoxidation and enzymatic oxidation can vary widely, ranging from 1 to 100 depending on their chemical structure [27]. During malting, there is a reduction in phenolic content, with catechin monomers being the most affected, as shown by Goupy et al. (1999) [33]. The antioxidant (+)-catechin and ferulic acid decreased the rate of formation of some carbonyl compounds during beer forced-ageing in the presence of air, but had no impact during the extended storage of beer at low levels of oxygen [4]. The beer produced from proanthocyanidin-free barley called Caminant was considered to be slightly inferior by a tasting panel compared to reference beers brewed from barley varieties cultivated under comparable conditions. This may be attributed to the deficient polyphenol level, particularly the catechin fraction, in the Caminant barley variety. As a result, this variety poses challenges in terms of flavour stability [40]. Even though the potential benefit of polyphenols to the colloidal stability of beer, by forming non-biological haze with proteins, is now largely recognised, their beneficial role for flavour stability is still an open question. To prove this, it was recently demonstrated that the partial removal of polyphenols by polyvinylpolypyrrolidone has no impact on flavour stability [41]. PCA analysis has revealed that the chemical composition and sensory characteristics of aged beer are affected by the varietal differences in barley [42]. The presence of natural polyphenols in barley has been found to have a positive impact on beer flavour stability. However, it should be noted that technological factors can also significantly influence beer flavour stability, as evidenced by the significant heterogeneity observed in the malt bed during industrial kilning.

Boivin et al. (1993) demonstrated that malt contains compounds that can inhibit the lipoxygenase activity of germinating barley, prevent lipid oxidation, and exhibit reducing power, according to various methods for evaluating antioxidant properties. The malt's reducing compounds are produced during germination and increase during the first stage of kilning, but decrease at higher temperatures. The amount of reducing compounds in malt depends on the barley cultivar and the kilning conditions applied [26]. The kilning regime not only affects the malt's antioxidant properties but also influences the colour and flavour profile of the final beer product [29].

Barley and germinating barley produce enzymes that exhibit antioxidant activity. One such enzyme is superoxide dismutase (SOD, EC 1.15.1.1), which catalyses the conversion of superoxide radicals to hydrogen peroxide, which is subsequently broken down into water and oxygen by catalase (CAT, EC 1.11.1.6). Together, SOD and CAT maintain oxygen in a stable, less reactive state by reducing the levels of superoxide and hydroperoxide. Barley contains both of these enzymes and their activities increase during germination.

They can also survive pale kilning regimes but are destroyed at mashing temperatures exceeding 65 °C [43]. Peroxidase (POD, EC 1.11.1.7) is a primary antioxidant that can protect against medium oxidation by removing hydrogen peroxide. However, malt POD can also oxidize endogenous barley phenolic compounds, such as ferulic acid, (+)-catechin, and (−)-epicatechin, which could have negative effects on beer quality [44]. The residual enzyme activities in malt depend on both the barley cultivar and the malting process. Natural antioxidant compounds in malt, such as phenolic compounds and MRPs, may play a significant role in inhibiting oxidative processes during malting and brewing. These antioxidants can inhibit lipoxygenase action during malting and mashing and decrease the autoxidation reaction during the brewing process and beer storage. While enzyme antioxidants can only act during malting and at the beginning of mashing, phenolic compounds and MRPs can act throughout the process and even after the beer has been stored. Therefore, careful selection of barley cultivars and malting regimes can help maximize the antioxidant potential of malt and improve beer quality.

4. Malt Pro-Oxidant Activity

Pro-oxidant malt compounds are primarily associated with the enzymes that are responsible for the breakdown of lipids. These enzymes include lipase (EC 3.1.1.3), lipoxygenase (LOX, EC 1.13.11.12), and the hydroperoxide-reactive enzyme system (Figure 2).

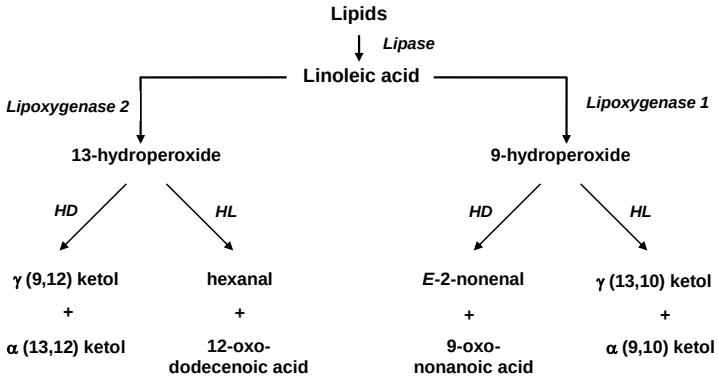

Figure 2. The enzymatic oxidation of lipids: lipase, lipoxygenase, and hydroperoxidase-reactive enzyme system. HL: hydroperoxide lyase. HD: hydroperoxide dehydrogenase (after [43]).

Oxidation of malt phenolic compounds by the catalytic action of polyphenol oxidase (PPO, EC 1.14.18.1) also occurs during the malting process. All these enzymes are found in most cereals, including barley [44], but they may also be synthesized by microflora developing during malting.

Pro-oxidant enzymes are primarily involved in lipid degradation. Lipase is the first enzyme to act on the ester bond between fatty acid and glycerol of triglycerides and diglycerides, releasing free fatty acids from lipids. Lipoxygenase catalyzes the oxidation of polyunsaturated free fatty acids, such as linoleic acid (C18:2), forming hydroperoxides. Lipoxygenase may also be involved in the creation of oxidative cross-linking between thiol-rich proteins via reactions, resulting in macromolecular reticulations that could alter the filterability performance of wort and beer, possibly affecting their quality [43]. The primary oxidation products of lipoxygenase activity, hydroperoxides, are decomposed into off-flavour compounds, such as unsaturated aldehydes, by hydroperoxide reactive enzyme systems, namely, hydroperoxide lyase and hydroperoxide isomerase (EC 4.2.1.92) [26]. High moisture content (above 40%) and low temperatures (below 60 °C) promote lipoxygenase (LOX) activity during the withering phase of kilning, resulting in the synthesis of E-2-nonenal and adduct formation. These nonenal adducts, also known as malt-RNP, which account for approximately 25% of the nonenal potential in the mash, can have a negative impact on the flavour stability of beer [45]. However, Carlsberg Research Laboratory developed a low-lipoxygenase barley cultivar in 2002, which expresses mutant LOX-1

protein. This barley variety can produce beer with significantly enhanced flavour stability and reduced levels of E-2-nonenal. Through mutation breeding, a LOX-1-null barley line was obtained, which can improve the flavour stability of beer without affecting other important beer qualities [46]. The results of a recent study clearly indicated that the LOX-less barley malt showed less nonenal potential than the control, and the beer brewed from the LOX-less barley malt contained much lower concentrations of trans-2-nonenal (T2N) and gamma-nonalactone, especially after the (forced or natural) aging of the beer, compared with the beer brewed under the same conditions using the control malt [47].

Polyphenol oxidase is able to catalyse the oxidation of polyphenols compounds with oxygen in very reactive quinonic compounds (Figure 3). In the oxidized state, they can cross-link and polymerize with proteins or cell-wall polysaccharides, directly influencing the formation of non-biological haze in wort and beer. Polyphenol oxidase is primarily responsible for enzymatic browning in fruits and vegetables. Enzymatic or chemical oxidation of polyphenols typically results in a loss of their antioxidant capacity. However, recent studies suggest that partially oxidized polyphenols may exhibit higher antioxidant activity than non-oxidized phenols [48].

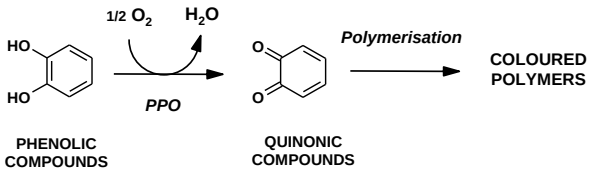

Figure 3. The action of polyphenol oxidase (PPO).

The pro-oxidant activity of malt extracts can also be attributed to flavonoids, procyanidins, and certain MRPs [29]. Many phenolic compounds act as antioxidants only at high concentrations, but at lower levels, they may have pro-oxidant effects [49]. Apart from their well-established antioxidant properties, MRPs may also exhibit pro-oxidant properties. Highly reactive radicals are generated in the initial stages of the Maillard reaction, and their disappearance is accompanied by the gradual development of browning. The level of these radicals depends on the intensity and duration of the heat treatment applied because at low temperatures, the reaction steps contributing to the formation of pro-oxidant compounds last longer than with high-temperature treatments [50]. High molecular weight browning compounds, generated by roasting barley, have been shown to act as pro-oxidants in metal-catalyzed oxidation reactions [51].

Figure 4 illustrates some possible routes of the pro- and antioxidant enzymatic activity in the malting and brewing process.

Through their sequential action, these enzymes are most active during the malting and mashing processes. Enzymatic activity is destroyed during the kilning and mashing steps, except for POD, which is a highly heat-stable enzyme. However, POD, which can oxidize phenolic compounds, appears to have limited action in the finished product due to the extremely low levels of hydrogen peroxide. In contrast, phenolic compounds and MRPs may play a significant role throughout the entire process and even after beer storage. Evidence has been provided for the inhibitory action of malt polyphenols on lipoxygenase (LOX) activity in finished malts. The anti-radical power, which is highly correlated with polyphenolic content, was found to be similar for both malt and barley, highlighting the essential role of barley's endogenous polyphenols on beer flavour stability [52]. The radical scavenging properties of highly polymerized phenolic compounds may also be effective against oxidative reactions during the malting and mashing stages. A deeper understanding of this issue could be achieved by investigating the mechanism by which malt polyphenols exert their protective action throughout the malting, mashing, or filtration steps against oxidative reactions.

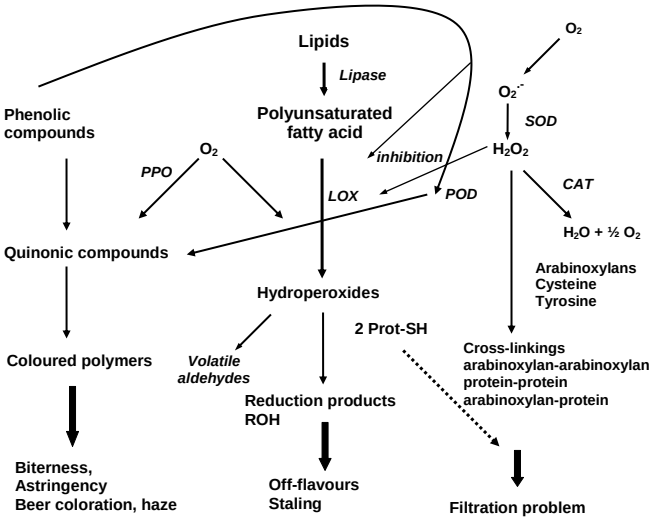

Figure 4. Implication of pro- and antioxidant enzymes in the malting and brewing process.

5. Concluding Remarks

The quality of malt can impact beer instability due to the presence of lipids, oxidative enzymes (such as lipoxygenase, hydroperoxide lyase, and hydroperoxide dehydrogenase), polyphenols, and phenolic acids. Polyphenols and phenolic acids present in malt are natural antioxidants capable of delaying, retarding, or preventing oxidation processes. Therefore, they are considered to have a significant effect on malting and brewing as inhibitors of oxidative damage. As a result, increasing attention is being directed toward the final properties of raw materials. For example, protecting the endogenous antioxidants present in barley during malting could increase the reduction potential of the brew, thus helping to inhibit oxidative processes that are detrimental to flavour stability and avoid the use of exogenous antioxidant compounds. Among the measured variables for malts, malt anti-radical power is the major contributor to beer flavour stability. In conclusion, it is clear that malt quality in terms of pro-oxidant and antioxidant activity plays a central role in beer flavour instability. This can be improved through a suitable choice of barley and malting process. Malt with low lipoxygenase activity, low residual nonenal potential, free phenolic compounds with high antioxidant activity, and a high amount of reducing compounds provide an excellent starting point.

Author Contributions: L.F.G. coordinated the study and contributed to the writing, editing, and correction of the manuscript. He is also the corresponding author of this article. I.M.F. contributed to the writing and editing of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Fundação para a Ciência e Tecnologia, grant number UIDB/50006/2020, UIDP/50006/2020, and PD/BD/135091/2017.

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.

References

1. Bamforth, C. *Beer: Tap into the Art and Science of Brewing*; Oxford University Press: Oxford, UK, 2003.
2. Carvalho, D.O.; Gonçalves, L.M.; Guido, L.F. Overall antioxidant properties of malt and how they are influenced by the individual constituents of barley and the malting process. *Compr. Rev. Food Sci. Food Saf.* **2016**, *15*, 927–943. [CrossRef]

3. Santos, J.R.; Carneiro, J.R.; Guido, L.F.; Almeida, P.J.; Rodrigues, J.A.; Barros, A.A. Determination of E-2-nonenal by high-performance liquid chromatography with UV detection assay for the evaluationof beer ageing. *J. Chromatogr. A* **2003**, *985*, 395–402. [CrossRef]
4. Walters, M. Natural Antioxidants and flavour stability. *Ferment* **1997**, *10*, 111–119.
5. Guido, L.F.; Fortunato, N.A.; Rodrigues, J.A.; Barros, A.A. Voltammetric assay for the aging of beer. *J. Agric. Food Chem.* **2003**, *51*, 3911–3915. [CrossRef]
6. Stewart, G.G. The production of secondary metabolites with flavour potential during brewing and distilling wort fermentations. *Fermentation* **2017**, *3*, 63. [CrossRef]
7. Murakami, A.A.; Goldstein, H.; Navarro, A.; Seabrooks, J.R.; Ryder, D.S. Investigation of beer flavor by gas chromatography-olfactometry. *J. Am. Soc. Brew. Chem.* **2003**, *61*, 23–32. [CrossRef]
8. Gijs, L.; Chevance, F.; Jerkovic, V.; Collin, S. How low pH can intensify β-damascenone and dimethyl trisulfide production through beer aging. *J. Agric. Food Chem.* **2002**, *50*, 5612–5616. [CrossRef] [PubMed]
9. Guido, L.F.; Carneiro, J.R.; Santos, J.R.; Almeida, P.J.; Rodrigues, J.A.; Barros, A.A. Simultaneous determination of E-2-nonenal and beta-damascenone in beer by reversed-phase liquid chromatography with UV detection. *J. Chromatogr. A* **2004**, *1032*, 17–22. [CrossRef]
10. Carneiro, J.R.; Guido, L.F.; Almeida, P.J.; Rodrigues, J.A.; Barros, A.A. The impact of sulphur dioxide and oxygen on the behaviour of 2-furaldehyde in beer: An industrial approach. *Int. J. Food Sci. Technol.* **2006**, *41*, 545–552. [CrossRef]
11. Ditrych, M.; Filipowska, W.; De Rouck, G.; Jaskula-Goiris, B.; Aerts, G.; Andersen, M.L.; De Cooman, L. Investigating the evolution of free staling aldehydes throughout the wort production process. *Brew. Sci.* **2019**, *72*, 10–17.
12. Reichel, S.; Carvalho, D.O.; Santos, J.R.; Bednar, P.; Rodrigues, J.A.; Guido, L.F. Profiling the volatile carbonyl compounds of barley and malt samples using a low-pressure assisted extraction system. *Food Control* **2021**, *121*, 107568. [CrossRef]
13. Van Waesberghe, J.W. Flavour stability starts with malt and in the brewhouse. *Brauwelt Int.* **2002**, *20*, 375–377.
14. Fickert, B.; Schieberle, P. Identification of the key odorants in barley malt (caramalt) using GC/MS techniques and odour dilution analyses. *Food Nahrung* **1998**, *42*, 371–375. [CrossRef]
15. Meilgaard, M.C. Flavor chemistry of beer. II. Flavor and threshold of 239 aroma volatiles. *Tech. Quart. Master. Brew. Assoc. Am.* **1975**, *12*, 151–168.
16. Guyot-Declerck, C.; François, N.; Ritter, C.; Govaerts, B.; Collin, S. Influence of pH and ageing on beer organoleptic properties. A sensory analysis based on AEDA data. *Food Qual. Prefer.* **2005**, *16*, 157–162. [CrossRef]
17. Wainwright, T. Diacetyl—A review. 1. analytical and biochemical considerations. ii. brewing experience. *J. Inst. Brew.* **1973**, *79*, 451–470. [CrossRef]
18. Briggs, D.E.; Hough, J.S.; Stevens, R.; Young, T.W. *Malting and Brewing Science: Malt and Sweet Wort*; Springer: Berlin/Heidelberg, Germany, 1982; Volume 1.
19. EBC. *Malting Technology: Manual of Good Practice*; Carl, F.H., Ed.; EBC: Nürnberg, Germany, 2000.
20. Belitz, H.D.; Grosch, W.; Schieberle, P. Springer Food chemistry 4th revised and extended edition. *Annu. Rev. Biochem.* **2009**, *79*, 655–681.
21. Mosher, M.; Trantham, K. *Brewing Science: A Multidisciplinary Approach*; Springer: Berlin/Heidelberg, Germany, 2017.
22. Dong, L.; Hou, Y.; Li, F.; Piao, Y.; Zhang, X.; Zhang, X.; Li, C.; Zhao, C. Characterization of volatile aroma compounds in different brewing barley cultivars. *J. Sci. Food Agric.* **2015**, *95*, 915–921. [CrossRef] [PubMed]
23. Bettenhausen, H.M.; Barr, L.; Broeckling, C.D.; Chaparro, J.M.; Holbrook, C.; Sedin, D.; Heuberger, A. Influence of malt source on beer chemistry, flavor, and flavor stability. *J. Food Res. Int.* **2018**, *113*, 487–504. [CrossRef]
24. Halliwell, B.; Gutteridge, J.M.C.; Aruoma, O.I. The deoxyribose method: A simple "test-tube" assay for determination of rate constants for reactions of hydroxyl radicals. *Anal. Biochem.* **1987**, *165*, 215–219. [CrossRef]
25. Van Gheluwe, J.E.A.; Yalyi, Z.; Dadic, M. Oxidation in brewing. *Brew. Dig.* **1970**, *45*, 70–79.
26. Boivin, P.; Clamagirand, V.; Maillard, M.N.; Berset, C.; Malanda, M. Malt quality and oxidation risk in brewing. *Proc. Conv. Int. Brew. Asia Pac. Sect.* **1996**, *24*, 110–115.
27. Boivin, P.; Allain, D.; Clamagirant, V.; Maillard, M.N.; Cuvelier, M.E.; Berset, C.; Richard, H.; Nicolas, J.; Forget-Richard, F. Mesure de l'activité antioxygène de l'orge et du malt: Approche multiple. *Proc. Congr. Eur. Brew. Conv.* **1993**, 397–404.
28. Maillard, M.N.; Soum, M.H.; Boivin, P.; Berset, C. Antioxidant activity of barley and malt: Relationship with phenolic content. *J. Food Sci. Technol.* **1996**, *29*, 238–244. [CrossRef]
29. Woffenden, H.M.; Ames, J.M.; Chandra, S.; Anese, M.; Nicoli, M.C. Effect of kilning on the antioxidant and pro-oxidant activities of pale malts. *J. Agric. Food Chem.* **2002**, *50*, 4925–4933. [CrossRef]
30. Samaras, T.S.; Camburn, P.A.; Chandra, S.X.; Gordon, M.H.; Ames, J.M. Antioxidant properties of kilned and roasted malts. *J. Agric. Food Chem.* **2005**, *53*, 8068–8074. [CrossRef] [PubMed]
31. Vanderhaegen, B.; Neven, H.; Verachtert, H.; Derdelinckx, G. The chemistry of beer aging—A critical review. *Food Chem.* **2006**, *95*, 357–381. [CrossRef]
32. Inns, E.L.; Buggey, L.A.; Booer, C.; Nursten, H.E.; Ames, J.M. Effect of modification of the kilning regimen on levels of free ferulic acid and antioxidant activity in malt. *J. Agric. Food Chem.* **2011**, *59*, 9335–9343. [CrossRef]
33. Coghe, S.; Vanderhaegen, B.; Pelgrims, B.; Basteyns, A.V.; Delvaux, F.R. Characterization of dark specialty malts: New insights in color evaluation and pro-and antioxidative activity. *J. Am. Soc. Brew. Chem.* **2003**, *61*, 125–132. [CrossRef]

34. Čechovská, L.; Konečný, M.; Velíšek, J.; Cejpek, K. Effect of Maillard reaction on reducing power of malts and beers. *Czech J. Food Sci.* **2012**, *30*, 548–556. [CrossRef]
35. Goupy, P.; Hugues, M.; Boivin, P.; Amiot, M.J. Antioxidant composition and activity of barley (*Hordeum vulgare*) and malt extracts and of isolated phenolic compounds. *J. Sci. Food Agric.* **1999**, *79*, 1625–1634. [CrossRef]
36. Chandra, C.S.; Buggey, L.A.; Peters, S.; Cann, C.; Liegeois, C. Factors Affecting the Development of Antioxidant Properties of Malts during the Malting and Roasting Process. *Hgca Proj. Rep.* **2001**. Available online: https://ahdb.org.uk/factors-affecting-the-development-of-antioxidant-properties-of-malts-during-the-malting-and-roasting-process (accessed on 14 April 2023).
37. Pascoe, H.M.; Ames, J.M.; Chandra, S. Critical stages of the brewing process for changes in antioxidant activity and levels of phenolic compounds in ale. *J. Am. Soc. Brew. Chem.* **2003**, *61*, 203–209. [CrossRef]
38. Moreira, M.M.; Morais, S.; Carvalho, D.O.; Barros, A.A.; Delerue-Matos, C.; Guido, L.F. Brewer's spent grain from different types of malt: Evaluation of the antioxidant activity and identification of the major phenolic compounds. *Food Res. Int.* **2013**, *54*, 382–388. [CrossRef]
39. Boivin, P.; Malanda, M.; Clamagirand, V. Evaluation of the organoleptic quality of malt. Evolution during malting and varietal influence. *Proc Congr. Eur. Brew. Conv.* **1995**, 159–168.
40. Back, W.; Forster, C.; Krottenthaler, M.; Lehmann, J.; Sacher, B.; Thum, B. New research findings on improving taste stability. *Brauwelt Int.* **1999**, *17*, 394–405.
41. Bushnell, S.E.; Guinard, J.X.; Bamforth, C.W. Effects of sulfur dioxide and polyvinylpolypyrrolidone on the flavor stability of beer as measured by sensory and chemical analysis. *J. Am. Soc. Brew. Chem.* **2003**, *61*, 133–141. [CrossRef]
42. Guido, L.F.; Curto, A.; Boivin, P.; Benismail, N.; Gonçalves, C.; Barros, A.A. Predicting the organoleptic stability of beer from chemical data using multivariate analysis. *Eur. Food Res. Technol.* **2007**, *226*, 57–62. [CrossRef]
43. Bamforth, C.; Clarkson, S.; Large, P. The relative importance of polyphenol oxidase, lipoxygenase and peroxidases during wort oxidation. *Proc. Congr. Eur. Brew. Conv.* **1991**, *23*, 617–624.
44. Boivin, P. Pro-and anti-oxidant enzymatic activity in malt. *Cerevisia* **2001**, *26*, 109–116.
45. Guido, L.F.; Boivin, P.; Benismail, N.; Gonçalves, C.R.; Barros, A.A. An early development of the nonenal potential in the malting process. *Eur. Food Res. Technol.* **2005**, *220*, 200–206. [CrossRef]
46. Hirota, N.; Kuroda, H.; Takoi, K.; Kaneko, T.; Kaneda, H.; Yoshida, I.; Takashio, M.; Ito, K.; Takeda, K. Brewing performance of malted lipoxygenase-1 null barley and effect on the flavor stability of beer. *Cereal Chem.* **2006**, *83*, 250–254. [CrossRef]
47. Yunhong, Y.; Huang, S.; Dong, J.; Fan, W.; Huang, S.; Liu, J.; Chang, Z.; Tian, Y.; Hao, J.; Hu, S. The influence of LOX-less barley malt on the flavour stability of wort and beer. *J. Inst. Brew.* **2014**, *120*, 93–98.
48. Manzocco, L.; Calligaris, S.; Mastrocola, D.; Nicoli, M.C.; Lerici, C.R. Review of non-enzymatic browning and antioxidant capacity in processed foods. *Trends Food Sci. Technol.* **2000**, *11*, 340–346. [CrossRef]
49. Yen, G.C.; Chen, H.Y.; Peng, H.H. Antioxidant and pro-oxidant effects of various tea extracts. *J. Agric. Food Chem.* **1997**, *45*, 30–34. [CrossRef]
50. Nicoli, M.C.; Anese, M.; Parpinel, M. Influence of processing on the antioxidant properties of fruit and vegetables. *Trends Food Sci. Technol.* **1999**, *10*, 94–100. [CrossRef]
51. Carvalho, D.O.; Øgendal, L.H.; Andersen, M.L.; Guido, L.F. High molecular weight compounds generated by roasting barley malt are pro-oxidants in metal-catalyzed oxidations. *Eur. Food Res. Technol.* **2016**, *242*, 1545–1553. [CrossRef]
52. Guido, L.F.; Curto, A.F.; Boivin, P.; Benismail, N.; Gonçalves, C.R.; Barros, A.A. Correlation of malt quality parameters and beer flavor stability: Multivariate analysis. *J. Agric. Food Chem.* **2007**, *55*, 728–733. [CrossRef] [PubMed]