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Changes in aroma composition and sensory properties provided by distiller's grains addition to bakery products

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ABSTRACT

The limited use of distiller's grains (DG) in the food industry result out of negative effects on texture and flavour. To investigate the odour, aroma volatiles in the common cereal based food system bread were analyzed. Therefore aroma volatiles in bread containing 0–20% DG were identified with Gas Chromatography-Olfactometry/Mass Spectrometry. Likewise, sensory properties were evaluated. As a result, 42 odour active compounds were identified in DDG bread. Phenylacetic acid and dimethyl-trisulphide are transferred from DG to bread crust and crumb, but not interfering bread aroma. After comparison of highest flavour dilution (FD) factors, 4-hydroxy-2,5-dimethyl-3(2H)-furanone (FD = 128) and 2-ethyl-3,5-dimethylpyrazine (FD = 128) were revealed in control bread crust, whereas 3-hydroxy-4,5-dimethyl-2-(5H)-furanone (FD = 512) and 4-hydroxy-23,5-dimethyl-3-(2H)-furanone (FD = 512) were revealed in 20% DG bread crust. Regarding bread crumb, 3-methylthiopropanal and 2-phenylethanol provided highest FD factors (FD = 32) in the control, whereas in 20% DG bread crumb 3-methylbutanoic acid, 2-ethyl-3,5-dimethylpyrazine and 3-hydroxy-4,5-dimethyl-2-(5H)-furanone provided FD factors ≥ 32 as well. Principal component analysis (PCA) of bread samples correlated to sensory attributes and important aroma volatiles revealed differences in odorant perception to the presence of 3-hydroxy-4,5-dimethyl-2(5H)-furanone and phenylacetic acid, with simultaneous absence of 2AP.

1. Introduction

In the 21st century sustainable engineering and a zero waste society become central topics of the global food industry. The growing world population will lead to a growing demand in food products and will cause deficits in the food supply chain. Within this discussion, the upcycling of byproducts gained much attention, due to the fact that 39% of food losses occur in the food manufacturing industry (Mirabella et al., 2014; van der Goot et al., 2016). Among the cereal manufacturing industry byproducts like bran from the milling industry, brewers spent grain out of the brewery or distiller's grains from the ethanol industry arise next to the main product.

With respect to its composition, distiller's grains (DG) represent a byproduct, not fully exhausted by now, since the amounts in dry matter are described up to 45% for neutral detergent fibre and 35% for protein (Rasco and Rubenthaler, 1990; Roth et al., 2014). To add value to this byproduct, DG can be a source for enriching food products with dietary fibre and protein. DG arise as main byproduct in the manufacturing process of fuel or beverage ethanol out of cereals like wheat or corn. Milled cereals are mashed and enzymes convert starch to yeast digestible carbohydrates. Subsequently, yeasts metabolise digestible carbohydrates to ethanol during fermentation. After distillation of ethanol, distiller's grains remain as a stillage, which is concentrated and subsequently dried to prolong its shelf life (dried distiller's grains, DDG). With regard to the production process, DDG mainly consist of outer grain layer components including the embryo and amounts of yeast cells remaining after the fermentation and distillation process. DDG contains especially high amounts of protein and dietary fiber, but only residual amounts of digestible carbohydrates (Rosentrater and Krishnan, 2006; Liu, 2011).

From a nutritional and sustainable point of view the utilization of DDG as food ingredient seems obvious. However, its application

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still isn't usual. The incorporation of DDG in food products was the topic of numerous studies during the 1980s and 1990s, especially regarding integration in cereal food products like bread and noodles. The results were not sufficient, because the addition of high fiber fractions is connected to some challenges and often linked to deficits in consumer acceptance of texture and flavour (Abbott et al., 1991; Bookwalter et al., 1984, 1988; Rasco et al., 1989). For instance, DDG addition in baguettes provides an aftertaste and leads to increased perception of sour, salty and bitter taste in comparison to the control (Rasco et al., 1989). Additionally, poor flavour was the reason for deficits of DDG in blended foods (Bookwalter et al., 1984). These sensory deficiencies were attributed to the characteristic and special aroma of DG (Rosentrater and Krishnan, 2006). However, a study providing information concerning sensory and chemical analysis on aroma composition in DDG enriched food products is still missing. In previous studies it was shown that the typical DDG odour shows high compliance to wheat processed products such as white wheat bread (Roth et al., 2014). The composition of flavour volatiles depends on the fact that DDG represents a thermal processed wheat product. So, the composition of flavour volatiles can match the bakery product and can provide new possibilities for including DG in food products.

The aim of this work was to provide insights into the sensory deficits occurring along with the application of DDG in bakery products and to identify components responsible for the typical flavour. For this reason amounts of 5, 10, 15 and 20% wheat flour were replaced by DDG from wheat and effects of DDG on sensory properties and the composition of flavour volatiles were investigated. After evaluation of sensory characteristics, volatile flavour compounds were isolated by means of Solvent Assisted Flavour Evaporation (SAFE) and identified with Gas Chromatography-Olfactometry/Mass Spectrometry (GC-O/MS). Key aroma compounds were classified by aroma extract dilution analysis (AEDA).

2. Materials and methods

2.1. Dried distiller's grains and raw materials for bread preparation

Dried distiller's grains (DDG) from wheat were purchased from Euro-Alkohol GmbH (Lüdinghausen, Germany). DDG were composed of 38.2% protein (AACC 46-16, N × 6.25), 3.6% fat (AACC 30-25), 3.5% ash (AACC 08-01), 46.8% total dietary fiber (AACC 32-05) on dry basis and 7.8% water (AACC 44-01) and is characterized by a water retention capacity of 54.1% (AACC 56-11). Flavour analysis was carried out using DDG of the same batch, to exclude influences through different composition or dryness. Before extraction of the volatile fraction, DDG was milled to particles <500 μm using an Ultra Centrifugal Mill of type ZM200 from Retsch (Haan, Germany).

Wheat flour type 550 was purchased from Rosenmühle (Ergolding, Germany) and was characterized by 10.6% protein (AACC 46-16, N × 6.25), 1.1% fat (AACC 30-25), 0.6% ash (AACC 08-01) on dry matter and 14.2% water (AACC 44-01). Further ingredients were sodium chloride (NaCl, Südsalz GmbH, Germany) and dry yeast of species *Saccharomyces cerevisiae* (fermipan red, Casteggio Lievitii srl, Casteggio, Italy). Analysis of flour and DDG were conducted in duplicate and presented as mean.

2.2. Chemicals

Chemicals were obtained from the following sources: Diethyl ether (≥99.5%) and anhydrous sodium sulfate (≥99.0) from Sigma-Aldrich (Taufkirchen, Germany), sodium carbonate (≥99.5%) from Merck (Darmstadt, Germany), sodium chloride from Avantor Performance Materials (Deventer, Netherlands) and hydrochloric acid (37%) from Roth (Karlsruhe, Germany). Reference standards of aroma compounds were purchased from commercial sources: Alfa Aesar, Karlsruhe, Germany; Merck, Darmstadt, Germany; Sigma-Aldrich, Taufkirchen, Germany; others were kindly provided from flavour companies (Firmenich, Switzerland; Symrise, Holzminden, Germany).

2.3. Preparation of dough and bread samples

Preparation of dough and bread samples was performed according to the procedure of Schirmer et al. with slight modifications (Schirmer et al., 2011). The recipe for control wheat bread preparation was 60.0 parts water, 2.0 parts sodium chloride and 1.6 parts dry yeast based on 100 g wheat flour (corrected to 14% moisture). To evaluate the influence of DDG on a control wheat bread, different amounts of wheat flour (0, 5, 10, 15, and 20%) were replaced by DDG. Water temperature was adjusted for dough end temperature of 28 °C and water amount was corrected for each DDG content for a maximum dough consistency of 500 Farinograph Units (FU). All ingredients were blended for 120 s at 100 rpm and mixed for 360 s at 200 rpm in a spiral kneader type 12 A-3 (Diosna Dierks & Söhne GmbH, Osnabrück, Germany). After resting for 15 min at room temperature, 250 g pieces of dough were hand-moulded, weighed in baking tins, kept in a proofing chamber for 30 min (30 °C, 80% relative humidity) and subsequently baked for 30 min at 230 °C in a multiple hearth-oven (Matador Store 12.8, Werner&Pfleiderer Lebensmitteltechnik Sachsen GmbH, Sohland, Germany). Each recipe was performed twice on different days, providing 4 independent bread loaves for analysis (n = 4).

2.4. pH measurement of bread samples

10.0 g of bread crumb were milled in a rotor mixer type GK 900 (Rotor Lips AG, Uetendorf, Switzerland) and mixed with 90 ml water. After homogenization the pH-value of the suspension was measured using a pH meter.

2.5. Isolation of flavour volatiles

30 min after baking, bread samples were separated in crumb and crust, cut into small pieces, frozen with liquid nitrogen and milled in a rotor mixer type GK 900 (Rotor Lips AG, Uetendorf, Switzerland). DDG enriched bread was exposed to an extraction with diethyl ether (DEE), in prior to distillation by SAFE. Therefore, 210 g of crumb or crust were mixed with 300 ml DEE, 0.5 ml of an internal standard (methyl decanoate in DEE with concentration of 0.83 g/L) were added for quantification. After 60 min the solvent was changed and the extraction continued for another 60 min. After filtration and concentrated to 50 ml. Subsequently the volatile fraction of the diethyl ether extract was isolated by means of Solvent Assisted Flavour Evaporation technique (Engel et al., 1999), dried over sodium sulfate and concentrated to 1 ml using a Vigreux column.

2.6. GC-Olfactometry-MS

Analysis of aroma extracts produced under 2.5 was carried out on a Trace 1300 GC directly coupled to an ISQ QD single quadrupole MS (Thermo Fisher Scientific, Dreieich, Germany). At the end of the capillary column, the effluent was split into a proportion of 2:1 using a 2-way-μ-split device (Gerstel, Munich, Germany) to the MS and the sniffing port (ODP 3, Gerstel, Munich, Germany). The sniffing port was heated to 250 °C and rinsed with humidified air, to avoid dehydration of nasal membranes of assessors. Samples were separated using a silica capillary column TG-5-MS (Thermo