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# Influence of citric acid incorporated in alginate casing on white efflorescence formation on dry fermented sausages (#422)

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### Introduction

The formation of white crystals on the surface, called white efflorescence, are a big issue for the meat processing industry because it is misjudged as microbial spoilage and therefore rejected by the consumer. It was identified that the formation is a physical mass transport phenomenon of acids and minerals from the core to the surface of the sausages [1]. Furthermore, as one of the main efflorescence causing (irreversible efflorescence type II) substances magnesium and lactate was identified. Moreover, due to the crosslinking of the alginate film with the divalent cation calcium in the form of calcium chloride (CaCl<sub>2</sub>)-solutions the formation could be enhanced. The effect of alginate casings on white efflorescence compared to natural and collagen casings was investigated by Walz et al. [2]. In the study the white efflorescence formation on the surface of the alginate casings (72.2%) was increased compared to collagen (48.3%) or natural (25.0%) casings. Furthermore, the diffusion of magnesium and calcium to the surface was significantly increased (p < 0.05) compared to the other casings. Therefore, in this study the effect of citric acid added to the alginate gel before co-extrusion on the white efflorescence formation was investigated, due to its ability to chelate divalent cations.

#### Methods

#### Production of dry fermented sausages:

The meat batter was composed of 20% frozen pork back fat SVIII (-18 °C), 45% frozen lean pork shoulder SII (-10 °C), and 35% minced lean pork shoulder SII (3 mm, 2 °C) purchased from a local wholesaler (MEGA eG, Stuttgart, Germany). Moreover, 0.1 g/kg starter culture (TEXEL® SA-308, mixture of Lactobacillus sakei, Staphylococcus carnosus and -xylosus), 0.5 g/kg ascorbic acid, 3 g/kg white pepper, 5 g/kg dextrose, and 28 g/kg nitrite curing salt (NCS, 0.5% nitrite) were added. The sausage batter was produced in a bowl chopper. The alginate gels (90% water, 10% alginate powder, Protanal<sup>®</sup> ME 5147, DuPont Nutrition & Health, Brabrand, Denmark) without chelator as a control and with the addition of 0.8, 1.1, and 1.4% of citric acid (Van Hees GmbH, Walluf, Germany). The sausages were manufactured with the ConPro co-extrusion unit (Albert Handtmann Holding GmbH & Co. KG, Biberach, Germany) with a casing thickness of 0.2 mm, caliber of 19, and a length of 270 mm. Subsequently, the co-extruded sausages were crosslinked with 25% of CaCl<sub>a</sub>. Afterwards, the sausages were fermented, lightly smoked, and dried (weight loss of 44%). After drying the sausages were packaged into vacuum bags under modified atmosphere (80%  $N_2$ , 20%  $CO_2$ ) and stored up to 8 weeks at 4 °C. For the chemical analyses the surface of the sausages were analyzed, therefore a layer of 0.6 mm thickness was cut off the sausages es with a food slicer (VS8A, Bizerba, Balingen, Germany).

Chemical and optical investigations:

Lactate, creatine and citric acid were determined by HPLC. Furthermore, the elements calcium and magnesium were determined by ICP-OES. The pH-value during the storage of 8 weeks were measured. For the image analysis 8 sausages were cut in half lengthwise, scanned and analyzed by ImageJ. The analyzes were done according to Walz et al. [1].

#### Results

The addition of all concentrations of citric acid significantly decreased (p < 0.05) the white efflorescence formation during the storage. The best results were achieved by the addition of 1.1% (17.55  $\pm$  4.85%) and 1.4% (13.09  $\pm$  1.64%) compared to the control (73.93  $\pm$  7.16%) after 8 weeks of storage (Figure 1). Citric acid showed a diffusion into the sausage during the storage. The amounts decreased by 40.09% (0.8%), 29.19% (1.1%), and 44.39% (1.4%) (Figure 2), but the diffusion of calcium and magnesium was not influenced during the storage compared to the control. However, the reduced efflorescence formation could be explained by the pH-values of the surface of the sausages. The pH-values of the samples with 1.1% and 1.4% were always significantly lower (p < 0.05) compared to the control. Initially after drying the pH-values were for 1.1 and 1.4% of citric acid at 4.73  $\pm$  0.03 and for the control at 4.90  $\pm$  0.01. Furthermore, the pH-values of all samples increased during the storage of the sausages which could be caused by the diffusion of citric acid into the sausage. Because of that, the efflorescence formation may not be inhibited because a comparable pH-value to the control sample  $(4.90 \pm 0.01)$  was reached after 6 weeks of storage  $(4.87 \pm 0.02$  for 1.1%; 4.84  $\pm$  0.02 for 1.4%). The critical pH-value for the formation of white efflorescences on dry-fermented sausages could be ~4.80 due to the biggest decline of the citric acid content on the surface. At lower pH-values the magnesium- or calcium lactate complexes could be soluble and therefore no crystals can be formed on the surface (Table 1).

#### Conclusion

The results of the study clearly demonstrate that the pH-value and the corresponding citric acid content of the surface influences the efflorescence formation and furthermore that pH-values below 4.80 could inhibit the for



# mation.

# References

1. Walz, F.H., et al. Journal of the Science of Food and Agriculture, 2017. 97(14): p. 4872-4879.

2. Walz, F.H., et al. LWT, 2018. 89: p. 434-440.

## Citric acid concentration (mg/g DM)

Figure 2 Citric acid contents (mg/g DM) of the sausages produced without or with the addition of citric acid.





#### Image analysis

Figure 1 Image analysis of the sausage surface with or without (control) the addition of citric acid.

Storage time (weeks)				
0	2	4	6	8
4.90 ± 0.01 <sup>a. B</sup>	5.03 ± 0.02 <sup>b. D</sup>	5.09 ± 0.04 <sup>bc. C</sup>	5.11 ± 0.04 <sup>bc. C</sup>	5.12 ± 0.04 <sup>c. C</sup>
4.89 ± 0.01 <sup>a. B</sup>	4.92 ± 0.01 <sup>a. C</sup>	4.98 ± 0.03 <sup>b. B</sup>	5.00 ± 0.01 <sup>b. B</sup>	5.01 ± 0.01 <sup>b. B</sup>
4.73 ± 0.03 <sup>a. A</sup>	4.80 ± 0.01 <sup>b. B</sup>	4.83 ± 0.02 <sup>bc. A</sup>	4.87 ± 0.02 <sup>c. A</sup>	4.95 ± 0.02 <sup>d. A</sup>
4.73 ± 0.03 <sup>a. A</sup>	4.76 ± 0.02 <sup>b. A</sup>	4.77 ± 0.01 <sup>a. A</sup>	4.84 ± 0.02 <sup>b. A</sup>	4.95 ± 0.02 <sup>c. A</sup>
	0 4.90 ± 0.01 <sup>a. B</sup> 4.89 ± 0.01 <sup>a. B</sup> 4.73 ± 0.03 <sup>a. A</sup> 4.73 ± 0.03 <sup>a. A</sup>	$\begin{array}{c ccccc} & & & & & \\ \hline 0 & 2 & & \\ \hline 4.90 \pm 0.01^{a.B} & 5.03 \pm 0.02^{b.D} \\ \hline 4.89 \pm 0.01^{a.B} & 4.92 \pm 0.01^{a.C} \\ \hline 4.73 \pm 0.03^{a.A} & 4.80 \pm 0.01^{b.B} \\ \hline 4.73 \pm 0.03^{a.A} & 4.76 \pm 0.02^{b.A} \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Storage time (weeks)   0 2 4 6   4.90 ± 0.01 <sup>a.B</sup> 5.03 ± 0.02 <sup>b.D</sup> 5.09 ± 0.04 <sup>bc.C</sup> 5.11 ± 0.04 <sup>bc.C</sup> 4.89 ± 0.01 <sup>a.B</sup> 4.92 ± 0.01 <sup>a.C</sup> 4.98 ± 0.03 <sup>b.B</sup> 5.00 ± 0.01 <sup>b.B</sup> 4.73 ± 0.03 <sup>a.A</sup> 4.80 ± 0.01 <sup>b.B</sup> 4.83 ± 0.02 <sup>bc.A</sup> 4.87 ± 0.02 <sup>c.A</sup> 4.73 ± 0.03 <sup>a.A</sup> 4.76 ± 0.02 <sup>b.A</sup> 4.77 ± 0.01 <sup>a.A</sup> 4.84 ± 0.02 <sup>b.A</sup>

<sup>a v</sup>: Significant differences (p < 0.05) during storage or 8 weeks of the single b A-D: Significant differences (p < 0.05) between the concentrations and control</p>

pH-values Table 1 pH-values (mean ± standard deviation) of the sausage surface layer produced without or with the addition of citric acid to the alginate gel during the storage of 8 weeks.



Notes