

CARBON MONOXIDE AS A SUBSTITUTE FOR NITRITE IN MEAT BATTER SYSTEMS

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Background

Nitrite (NaNO₂) and nitrate (NaNO₃), a precursor to nitrite, are widely used as additives in processed meat for enhancing colour and other properties of the products. Due to the risk of formation of carcinogenic compounds, finding alternative additives that can replace or reduce the addition of nitrite are highly desirable (Pegg and Shahidi, 2000). Carbon monoxide (CO) binds strongly to the muscle pigment myoglobin creating stable, bright red carboxymyoglobin. CO can be safely used in concentrations below 1 % in fresh meat packages, or in similar or higher concentrations for pretreatment of fresh meat (Sørheim *et al.*, 1997). Carboxymyoglobin has a higher denaturation temperature than other forms of myoglobin, e.g. deoxymyoglobin (Hunt *et al.*, 1999; Sørheim *et al.*, 2001), thus having a potential use as a colourant in typical cooked meat products.

Objective

The main objective was to study the effect of replacing nitrite with CO on the colour of cooked meat batter systems.

Materials and methods

The study was a multifactoral design with a total of 44 batches including:

- colour processes (4): CO gas flushing directly to batter (CO-D), CO pretreatment of raw materials (CO-R), addition of nitrite to batter (N), no CO/nitrite as control (C)
- meat sources (2): semimembranosus muscles of pork or beef
- antioxidants for CO-D and CO-R (4): ascorbic acid, phosphate, ascorbic acid + phosphate, none

- sodium chloride level for CO-D and CO-R (3): 0, 1.4 and 2.8 %

The design was unbalanced with some factors considered more important than others. Significance testing was performed by univariate and multivariate (Langsrud, 2002) analysis of variance. Effects were illustrated by least square means adjusted for unbalance.

The basic batter receipe consisted of:

- 70.0 % meat
- 24.4 % water
- 1.4 % NaCl
- 3.5 % native potato starch (Hoff, Gjøvik, Norway)
- 0.7 % Na-caseinate (Tine, Oslo, Norway).
- The following ingredients were added to some batches:
- 85 ppm NaNO₂
- 500 ppm ascorbic acid
- 0.3 % sodiumtripolyphosphate (A.B. Corneliussen, Oslo, Norway)

The raw batters contained on average 16.4 % protein, 1.4 % fat, 76.9 % water and 2.8 % carbohydrates. Total batter weight was 1.430 kg.

Fresh meat was ground twice through a 4 mm plate. Meat for the CO-R treatment was placed in polyamide pouches, compressed to < 5 mm, packaged in 1 % CO/ 99 % N₂ with < 0.2 % residual O₂ and stored at 3 °C



for 4 and 5 days for pork and beef, respectively. The meat pouch was turned at 2 days of storage to access gas from both sides. Batters were prepared in a Stefan UM5 chopper (A. Stephan u. Söhne, Hameln, Germany) with a lid and double bladed knives with a chopping time of 3 min and 20 sec. For CO-R, pretreated meat with CO was used without supply of CO in the chopper. Meat for CO-D was not pretreated with CO, but the batters were flushed with 1 % CO/ 99 % N₂ at 2 bars for the last 2 min of the chopping. All batters were filled in 50 ml polyethylene tube casings of 28 mm in diameter, centrifuged at 2000 rpm for 5 min, stored overnight at 3 °C, heated for 30 and 40 minutes in circulating water baths at 80 and 100 °C, respectively (the latter 8 batches only), chilled in ice water, and stored at 3 °C for 3 hours. Core temperature after cooking was measured with a 1 mm needle thermometer (Teck Instrument AS, Tranby, Norway). Casing was peeled off the cooked products, which were then sliced vertically in duplicate halves of 15 mm height for instrumental and visual colour analyses taking place at 0, 15 and 60 min of air exposure at 20 °C.

In a small additional experiment, two fermented batters of 1 kg each were prepared of beef *semimembranosus* muscle (94.5 %), dextrose (0.7 %), starter culture, NaCl (4.5 %), and ascorbic acid (500 ppm). In one batter, 180 ppm NaNO₂ was added, while the other batter was flushed with 1 % CO/ 99 % N₂ (see above for details). The batters were stored in 50 ml tubes for 6 days at 20 °C.

L*a*b* values (lightness, redness, yellowness) were measured with a Minolta Chroma Meter CR-300 (Minolta Camera Co., Osaka, Japan) with an 8 mm viewing port and a D_{65} -illuminator. Visual colour evaluation was performed by two trained assessors using a 5 point scale where 1 = very red/pink and 5 = extremely gray/brown. Denaturation of myoglobin was analysed by the method of Krzywicki (1979) (8 batches, each raw and at 80 °C). pH of the raw as well as the fermented batters was analysed with an Ingold Xerolyt gel electrode (Mettler-Toledo, Greifensee, Switzerland).

Results and discussion

Figs. 1 and 2 demonstrate a* values of pork and beef batters, respectively, heated into 80 °C, (actual core temperature was 79.5 °C), and exposed to air for 0, 15 or 60 min. Fig 3. shows the b* values for both pork and beef batters cooked to 80 °C. Fig. 4 demonstrates visual colour score of the batters at 80 °C. Immediately after slicing, the CO-D samples with CO gas flushing were more red with higher a* values than N samples on beef (p<0.05), but similar to the a* values on pork. However, after 15 and 60 min CO-D samples lost more redness than N in both species. The results of the visual colour evaluation corresponded to the a* values. Initial yellowness values (b*) were lower for CO-D than N beef samples (p<0.05), but were not different anymore at 15 and 60 minutes of O₂ exposure. CO-D samples were slightly lighter, expressing L* values of about a unit higher than the N samples at all measuring points (results not shown).

The CO-D gas flushing seemed to effectively replace O_2 with CO and bind to myoglobin in the final batters. The CO-R pretreatment was less efficient than direct flushing in producing a red colour of the samples, as shown in Figs. 1 - 4. Based on visual examination of the CO-R pretreated raw materials, 100 % of the pork and 80 - 90 % of the beef pigments were in the state of carboxymyoglobin. Despite the almost complete saturation of the meat pigment with CO, exchange of CO with O_2 during chopping was the likely cause for the less intense redness after cooking of CO-R samples. Although the red colour of CO-treated samples faded during air exposure, the colour could perhaps be maintained by keeping the samples in an anaerobic environment. The level of NaCl or the use of additives, either as ascorbic acid, phosphate or ascorbic acid + phosphate, did not much affect the colour of the final cooked batters of CO-D and CO-R (results not shown). The pH of the raw batters without additives was 5.51. Addition of phosphate increased the pH of the batter by 0.10 unit (p<0.05). Myoglobin denaturation at 80 °C was in the range 73 – 81 % for pork and 91 – 95 % for beef batters, respectively, with no apparent differences between CO-D, N and C samples. These results suggest that carboxymyoglobin denaturates to about the same extent as nitrosomyoglobin at 80 °C.

At 100 °C (actual core temperature was 98 °C), initial a* values of CO-D beef samples were slightly lower (about a unit) than at 80 °C, yet expressing a bright red colour (results not shown). However, pork CO-D samples gave approximately 2.5 units lower a* readings, and were clearly paler at 100 °C than the same samples at 80 °C.



In the fermented beef batters, pH was reduced from appr. 5.4 to 4.5 during fermentation. CO flushing produced a brighter red colour into the fermented samples than nitrite, but the colour of the CO sample faded away along with exposure to air (results not shown).

Conclusions

Direct flushing of pork and beef batters with 1 % CO produced an initial bright red colour into samples cooked into 80 °C. The internal colour of these samples immediately after slicing was equally or more intensely red than samples treated with nitrite. Pretreatment with 1% CO to raw materials that were later used for batter production, resulted in less efficient colour formation than the flushing of gas during chopping, probably due to exchange with O_2 during batter blending. Beef seemed to be more responsive than pork to colour improvement by CO flushing and pretreatment. The lack of colour stability of CO samples in O_2 exposure needs to be addressed further, perhaps with new processes or additives to counteract pigment oxidation.

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Figure 1. a* redness values of pork batters cooked to 80 °C and exposed to air for up to 60 minutes. Symbols: $\Delta = CO$ flushing of batters (CO-D), $\nabla = CO$ pretreatment of raw materials (CO-R), = nitrite (N), o = no CO/nitrite as control (C).





Figure 2. Redness values (a*) of beef batters cooked into 80 °C and exposed to air for up to 60 minutes. For symbols, see Fig. 1.



Figure 3. Yellowness values (b*) of pork and beef batters cooked into 80 °C and exposed to air for up to 60 minutes. Pork = solid lines, beef = dashed lines. For symbols, see Fig. 1.



Figure 4. Visual colour evalution of batters cooked to 80 °C and exposed to air for up to 60 minutes. Colour score (cs): 1 = very red/pink, 2 = some red/pink, 3 = slightly red/pink, 4 = some gray/brown, 5 = extremely gray/brown. For symbols, see Fig. 1.