The Stability and Distribution of Emulsifiers in Frankfurter-type Sausage Batters

H. WAGNER
Federal Centre for Meat Research, D-8650 Kulmbach, Germany

SUMMARY

The chemical stability and distribution of monoglycerides (glycerolmonooleate and -monopalmitate) and lecithin has been examined by means of radiotracer compounds in order to elucidate their mode of action during the process of manufacturing frankfurter-type sausages. The low "mobility" of the emulsifier molecules points to the colloidal system of a suspension (solid in the batter) in the meat "emulsion". There is no indication of the presence of emulsifiers in phase boundary areas of fat and water.

These facts support the theory, that lecithin molecules bind to proteins with the consequence of inhibiting the formation of a network, thus lowering the water holding capacity and quality of the product. There were no chemical changes in the structure emulsifiers during the process of manufacturing frankfurter type sausages.

INTRODUCTION

Emulsions are disperse systems of non-miscible liquids, one of which is dispersed very finely in the other one. Generally these disperse systems are very unstable, because the interfacial tension in the system can be reduced by the fusion of the droplets with the consequence of a state of reduced energy. Their stability can be improved by emulsifiers which contain polar and unpolar chemical groups in one molecule and therefore are localized in the phase boundary surfaces.

During the process of manufacturing frankfurter type sausage a water containing phase (meat and ice) is mixed with the fat it is done producing an emulsion. Because the fat is solid under the conditions in the bowl cutter, this batter can hardly be characterized as an emulsion, but rather called a suspension (HAMM, 1973). It is possible, however, that there exists a suspension below a certain temperature, but an emulsion, when it is heated (GIRARD et al, 1983).

It is questionable if emulsifiers under these conditions are effective. Indeed earlier examinations showed that the addition of emulsifiers does not necessarily cause a stabilisation of the batter (HONIKEL and HAMM, 1983a; DENK and HONIKEL, 1986) Obviously only monoglycerides with long-chain fatty acids of 16 or more carbon atoms exert a stabilizing influence. An increasing portion of unsaturated fatty acids in the glyceride also reduces the batter stability.

An addition of lecithin (in Germany not allowed as an additive for meat products) also has consequences contraditory to the theory of emulsifiers. An addition of 0.5% natural lecithin causes a significant increase of jelly deposit (HONIKEL, 1982; HONIKEL and HAMM, 1982, 1983b; HONIKEL et al, 1982). In order to explain this negative effect of lecithin HONIKEL developed the working hypothesis that lecithin molecules bind to the proteins with the consequence of inhibiting the formation of a protein network thus lowering the water holding and fat binding capacity and the quality of the product. Without lecithin within the course of the heating process a coherent network is formed in the batter, where water and the previously added fat are enclosed (HONIKEL, 1982; HONIKEL and HAMM, 1983a).

The distribution of the additives can be examined in a product free of cookout as well as in a product containing cookout. The application of radiotracer emulsifiers offers the following advantages: On account of a fraction of at least 30% fat in the product and an added amount of only 0.5% of emulsifier, the emulsifier stands a 60-fold amount of chemically related lipid substances. These have to be separated by time consuming chemical operations in order to avoid interference with the quantitative determination of the emulsifiers. The use of radiotracer compounds, however, simplifies the analytics, because the decaying atoms in the labelled molecules allow a very sensitive determination of amount and localization.

But there are ale obstacles. Tritium atoms in chemically instable positions under suitable conditions can substitute with surrounding protons (mainly from water). Furthermore it is possible that the ester bonds in monoglycerides or lecithin are cleaved with or without involvement of enzymes, releasing the labeled fatty acids (hydrolysis). There exists also the possibility that the unsaturated oleic acid respectively the corresponding monooleate is oxidized and cleaved. In all cases an examination of the distribution of radioactivity in the batter leads to misinterpretations. Accordingly the stability of the used radiotracers has to be checked.

MATERIALS AND METHODS

In C-9, 10-position labeled palmitic respectively oleic acid have been used as precursors. By reaction of palmitoylchloride respectively oleoylchloride with glycerol the glycerolmonoesters were **synthesized** from palmitoylchloride and the cadmium-

chloride complex of glycerophosphatidylcholine resulted **lecithin** (1,2-dipalmitoylphosphatidylcholine). The products were purified by thin layer chromatography.

The activity concentrations of the labeled compounds have been determined with **liquid scintillation counters**. Samples of the jelly or fat phase could be assayed without further preparation. The protein containing part which remained after drying and extraction of fat tissue was treated with tissue solubilizers. Both components of the residual batter (fat and protein fraction) were assayed separately.

By the use of a **thin layer scanner with radioactivity detector** the yields of different synthesis reactions were compared, the purity of the reaction products tested and their stability under the conditions of meat processing examined.

By **autoradiography** which depends on the sensitivity of photographic emulsions against radiation, the distribution patterns of radiotracer substances can be made visible. 8 um thin layer cuts of the spiked sausage were covered with a few um thin layer of a photographic emulsion which was developed and fixed after exposition times of several weeks. The thin layer cuts were stained through the gelatin layer.

In order to check how strong the tritium atoms are bound to the emulsifier molecules, batters prepared with labeled emulsifiers and heated under the usual conditions were dried with P_2O_5 without direct contact. Then the tritium activity of the resulting phosphoric acid and of the dried batter were determined. In the case of monopalmitate and lecithine only about 0.03% of the used activity was found to be in the phosphoric acid. Thus these substances proved to be very useful.

In a corresponding experiment regarding the monooleate, 0.3% of the oleate tritium converted with water to HTO (one proton exchanged with tritium). This slightly higher lability of the tritium bond may be caused by the neighbouring double bond or by the oxidation of a small amount of the monooleate emulsifier.

In order to find out whether the additives are hydrolyzed during the manufacturing of the product, dried portions of the cooked mixture (with high specific radioactivity) were extracted with chloroform. After the separation of the extract by thin layer liquid chromatography the plates were scanned.

The preparation for autoradiography contained 48.1% pork, 30% ice, 20% pork back fat and 1.9% salt. The batter was manufactured at 15° C and heated at 80° C for 1 h. The preparations for liquid scintillation counting released deposits of jelly and fat. So it was possible, to determine the distribution of the emulsifiers on the fractions of fat, jelly and remaining batter. To this purpose a mixture of 42.1% pork, 26.3% ice, 30% pork back fat and 1.6% salt was prepared at 30° C and heated at 90° C.

Table 1: Distribution of radioactive emulsifiers in the parts of the sausage mixture

	deposits		batter without deposit		
	jelly	fat	total	protein	fat
monopalmitate					
weight %	23.0	2.5	74.5		
activity %	.07	15.7	84.3	8.0	76.3
monooleate					
weight %	22.7	7.9	69.4		
activity %	0.1	11.7	88.2	3.0	85.2
lecithin					
weight %	25.0	15.4	59.6		
activity %	0.3	5.9	93.8	41.8	52.0

RESULTS AND DISCUSSIONS

During the investigations about the stability of the emulsifiers indications of a hydrolysis of the glycerol esters could not be found. Also potential fragments of the oxidation of oleic acid (autoxidation products) could not be detected. Thus it can be assumed that the used additives remain unchanged during the technological process.

Liquid scintillation counting of the products had the following results (table 1): In the jelly the smallest part of all emulsifiers could be found actually more of lecithin (0.3%) than of monooleate (0.1%) or monopalmitate (0.07%). Despite an identical recipe and negligible amounts of added emulsifiers the composition of the products could not exactly be reproduced. In the preparations with lecithin a fat deposit of 15.4% resulted compared with 7.9% in case of monooleate and 2.5% in case of monopalmitate. The remaining batter in all cases contained the largest part of the emulsifiers. In spite of the smaller fraction of weight in the case of lecithin (59,6%) compared to monooleate (69.4%) or monopalmitate (74.5%) there were 93.8% of lecithin in the remaining batter compared with 88.2% of monooleate and 84.3% of monopalmitate. After the extraction of the remaining batter with ethanol/ether and chloroform/methanol in all three cases on account of the same recipe the same amount of protein remained, in the preparation with lecithin, however, it contained considerably more radioactive material (41.8%) compared to monooleate (3%) respectively monopalmitate (8%). In all preparations the fat in the remaining batter proved to be the component with the biggest amount of emulsifier. It contains, however, more monoglyceride (monopalmitate: 76.3%, monooleate: 85.2%) than lecithin (52%). Obviously there can be found less lecithin in the fat part than monoglycerides.

The **autoradiographs** of the products without deposits are reflecting these relations. When a preparation was spiked with 3 MBq tritiated monopalmitate after an exposition time of at least 3 weeks spots of silver grains were visible clearly above the fat particles in the sausage microstructure (fig. 1). The autoradiographs from the batter produced with lecithin showed no concentrations of silver grains above the fat particles, they were distributed more uniformly.

Thin layer cuts and also autoradiographs have been made from the unheated spiked batter. In case of both emulsifiers accumulations of radioactivity are distributed on only a part of the fat particles. Within the fat particles not always homogeneous distributions of the labeled substances exist. Flow figures can be recognized within the particles (fig. 2).

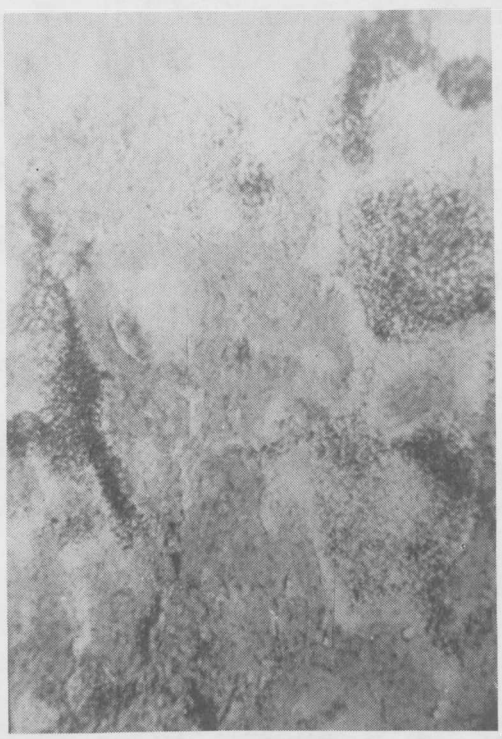

Fig. 1: Autoradiography of a thin layer of a frankfurter-type sausage made with labelled monopalmitate

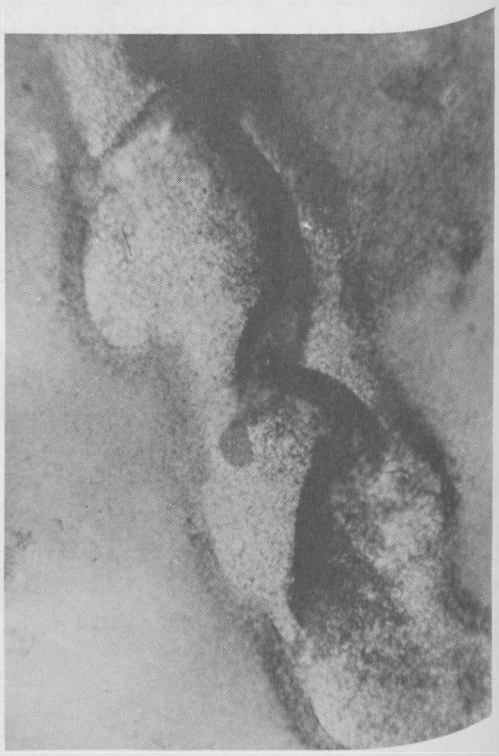

Fig. 2: Autoradiography of a thin layer of a frankfurter-type sausage made with labelled monopalmitate showing a flow pattern within a fat particle

Caused by the method of addition in form of a fat-water-mixture, the emulsifiers in the unheated batter are first of all concentrating in fat particles. The inhomogeneous distribution of the emulsifiers molecules as in the raw batter as within the particles themselves is caused by an only small mobility of molecules in the fat phase. This points to a suspension (solid fat in water). In the droplets of an emulsion the emulsifier should concentrate in the phase boundary surfaces. Due to the immobility of the molecules at this stage their emulsifying potential can not become apparent. Heating of the batter enables diffusion processes to take place, the emulsifier molecules can move to positions adequate to their chemical properties. Only at this stage between the liquefaction of the fat particles on one side and their immobilisation by coagulating proteins on their surface on the other side a stabilisation via a true emulsion should be possible.

The monoglyceride emulsifiers are concentrating in the fat particles of the batter, they are clearly more lipophilic than lecithin. Unlike lecithin they can be extraced quite well together with the fat. This fact points to a comparatively strong binding of lecithin to the components of the remaining batter particularly to the protein fraction. A link-up to low molecular water soluble proteins or dissolving in the aqueous phase can be excluded on account of the low emulsifier content of the jelly. In accordance with the mentioned working hypothesis it can be supposed that lecithin is bound to the proteins which are forming the structure of frankfurter type sausages.

A concentration of emulsifier molecules along the phase boundary surfaces could not be proven under the conditions of the autoradiography. The molecules are distributed uniformly within the fat particles though the amounts of substances used are very small (0.05% or 50 ppm). This does not exclude, however, that a noticeable amount of molecules is spread over the surface of the fat droplets where they can develop their emulsion stabilizing effect. Glycerolmonooleate differs less clearly from the monopalmitate than lecithin regarding its distribution in the batter. Thus an explanation of stability reducing effect of monooleate does not exist at present. It must be stressed, however, that the monooleate synthesized for these experiments had been of high chemical purity and protected against oxidation. Commercial emulsifiers stored under poor conditions might undergo autoxidation processes with reaction products that are very detrimental to product stability.

REFERENCES

DENK, G. and HONIKEL, K.O. (1986): Über die Wirkungsweise von Glyceridemulgatoren, Diphosphat und Citrat in Brühwurstbräten. Mitteilungsblatt der Bundesanstalt für Fleischforschung, Kulmbach **92**, 6907-6913.

GIRARD, J.P., DANTCHEV, S. and CALDERON, F. (1983): Beziehungen zwischen Temperatur sowie Zerkleinerungsgrad beim Kuttern und der Struktur von Brühwurstbrät. Fleischwirtschaft **63**, 909-914.

HAMM, R. (1973): Die Bedeutung des Wasserbindungsvermögens des Fleisches bei der Brühwursttherstellung. Fleischwirtschaft **53**, 73-81.

HONIKEL, K.O. (1982): Einfluß von Emulgatoren auf Brühwurst. Fleischwirtschaft **62**, 1390-1396.

HONIKEL, K.O. and HAMM, R. (1982): Der Einsatz von Emulgatoren bei der Herstellung von Brühwurst - III. Lecithine: Einfluß von Kutterzeit und Kuttertemperatur. Fleischwirtschaft **62**, 1332-1336.

HONIKEL, K.O. and HAMM, R. (1983a): Studies on the mode of action of emulsifiers in cooked sausages. Proceedings des 29. Europäischen Fleischforscherkongresses, Vol. 2, D.7, 496-502.

HONIKEL, K.O. and HAMM, R. (1983b): Untersuchungen zur Wirkungsweise von Emulgatoren bei der Brühwursttherstellung. Mitteilungsblatt der Bundesanstalt für Fleischforschung, Kulmbach **80**, 5474-5479.

HONIKEL K.O. and HAMM, R. (1983c): Einsatz von Emulgatoren bei der Herstellung von Brühwurst - IV. Lecithine: Einfluß der Salzkonzentration und des pH-Wertes. Fleischwirtschaft **63**, 1320-1327.

HONIKEL, K.O., PYRCZ, J. and HAMM, R. (1982): Verwendung von Emulgatoren bei der Herstellung von Brühwurst - II. Lecithine: Einfluß der Brätzusammensetzung. Fleischwirtschaft **62**, 507-510.