

Sorption of Volatile Flavor Compounds by Microcellular Cereal Starch

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Wheat starch based microcellular foam (MCF) forms of (dry) starch possess a significant percentage of micropores in the range of 5–14 Å. The present study confirmed earlier preliminary studies that MCF starch (in a 0.25–1.0 mm diameter bead form) is effective in sorbing and lowering the headspace partial pressure of many volatile compounds in a manner similar (although less efficient) to that exhibited by other microcavity sorbants such as charcoal. It was found that the proportion of polar compounds sorbed was much greater than the proportion of nonpolar compounds. A major portion of the sorbed volatile compound was readily displaced from the MCF microcellular starch by the addition of water. These properties make this form of edible starch a potential useful carrier of flavor compounds for dried foods.

Keywords: *Starch; microcellular foams; flavor compounds; sorption*

INTRODUCTION

Starch-based microcellular foams (MCF) are a porous dry form of starch produced from wheat and corn starch as described previously (Glenn and Irving, 1995; Glenn et al., 1996). Briefly, this involves gelatinization of the starch in hot (>90 °C) water, cooling the starch (to 5 °C) to form a gel, displacement of the water within the gel with ethanol, and removal of the ethanol by drying. The product used in the present work was in bead (0.25–1 mm in diameter) form. Scanning electron micrographs (Glenn et al., 1996) showed that this form of starch had a high percentage of pores in the range of 0.25–0.5 μm, with some as large as 2 μm and indications of smaller pores not measurable by scanning electron microscopy. Measurement of pore size using argon in a Horvat–Kawazoe cumulative volume plot showed pores in the range of 5–14 Å with a total volume of 0.057 mL per gram of starch for this range (G. M. Glenn, unpublished results, 1995).

Preliminary experiments with the MCF starch showed that it sorbed a number of volatile compounds, lowering their partial pressure in the headspace above the MCF starch many times (Glenn and Stern, 1997).

Studies were reported recently on sorption or binding of volatile compounds by ordinary starch powder by Hau et al. (1996), but the degree of lowering (50–80%) of the headspace partial pressure was considerably less than that found for the MCF starch.

Spray-drying and extrusion methods of binding volatile flavor compounds with carbohydrate materials are well-known (Reineccius, 1989). With such compounds the partial pressure and hence evaporation rate are lowered by being surrounded (encapsulated) by carbohydrate walls. The use of edible microporous sorbants such as MCF starch allows a different approach to the binding of flavor compounds, the partial pressure and evaporation rate being reduced by sorption.

MATERIALS AND METHODS

Materials. The MCF starch was prepared using the general method described previously (Glenn and Irving, 1995) from wheat starch. Preparation of the bead form required injection of the hot (90 °C) starch gel melt into chilled vegetable oil. The beads were collected in an ethanol/water layer and equilibrated for 24 h each with 2 volumes of pure ethanol. Besides displacing the water, this also served to remove any vegetable oil. The beads were dried by heating in an oven at 80 °C. The beads were 0.25–1 mm in diameter (~25–100 mesh). Analysis showed that the beads contained <0.01% oil and 10% moisture. The ordinary wheat starch used for comparison (and for preparation of the MCF) was Midsol 50 from Midwest Grain Products, Inc., Atchison, KS, and contained 9–12% moisture.

Volatile compounds were obtained from reliable commercial sources or synthesized according to well-established methods, and their purity was checked by capillary gas chromatography (GC) and mass and infrared spectrometry. Activated charcoal was 4–12 mesh and obtained from Aldrich Chemical Co. Tenax, 60–80 mesh, a porous polymer gas chromatography adsorbent, was obtained from Alltech Associates.

Determination of Headspace Partial Pressure Ratio. Five hundred milligrams of MCF starch beads was placed in a 125 mL Pyrex flask that had a hole ~2 mm in diameter halfway up the wall of the flask. The hole was covered with three layers of slightly stretched Teflon tape, which acted as a septum. Pure (PTFE) Teflon tape has the property of adhering to clean Pyrex glass sufficiently enough to close the hole so that it is gastight with the insignificant pressure drop across it. Teflon tape was used in preference to silicone rubber because it is well-known that silicone (and other) rubbers are good sorbants of organic volatiles. The experiments were conducted at a room temperature of 22 °C. A sample (5.0 μL) of the compound was placed on the floor of the flask near the beads and the flask immediately closed with a Pyrex stopper. For comparison, an identical flask was prepared containing 500 mg of ordinary wheat starch powder (Midsol 50) instead of the MCF starch. An identical sample of the test compound was added to the comparison flask. The flasks were allowed to stand at room temperature (22 °C) for 30 min. A sample of headspace atmosphere (1.0 mL) was then drawn out of one flask, with a gastight glass syringe fitted with a 25 gauge (~0.5 mm o.d.) needle, through the Teflon tape covered holes and

Table 1. Ratio of Partial Pressure (p) of Compounds in Headspace of Flask with MCF Starch to That (p^0) in Reference Flask with Ordinary Starch (Which Equals the Corresponding GC Peak Area Ratio)

compound	p/p^0	compound	p/p^0
dimethyl sulfide	0.91	hexyl acetate	0.03
decane	0.71	octanol	0.02
(S)-(-)-limonene	0.34	(Z)-3-hexenal	0.02
benzaldehyde	0.11	2-octanone	0.01
isobutyl cyanide	0.11	3,5-dimethylpyridine	0.01
3-pentanone	0.07	2,5-dimethylpyrazine	0.008
acetophenone	0.05	2-ethyl-3-methylpyrazine	0.007
hexanal	0.03		

^a Compounds were added in amounts of 5.0 μ L of compound to 0.50 g of MCF beads (~1%) or ordinary starch in a 125 mL Pyrex flask.

injected into the gas chromatograph (GC). At a suitably spaced time interval (~15–30 min, to allow time for the first GC peak to emerge) a similar sample was drawn out of the second flask and injected into the GC. Samples from the MCF starch flask and the comparison flask were injected alternately. Three samples from each flask were taken for each compound, and the mean was found from the GC peak area results. The ratio of the GC peak areas for the MCF headspace to that for the ordinary starch headspace was then determined. Because the partial pressures (and concentration) are proportional to the GC peak areas, this ratio is the same as that of the partial pressures.

GC. The GC instrument used was an HP 5890 with a flame ionization detector and a 60 m \times 0.32 mm i.d. fused silica capillary column coated with DB-1. The GC oven temperature was kept constant for each comparison, but the actual temperature used depended on the compound.

RESULTS AND DISCUSSION

Experiment Design. The method as outlined in detail under Materials and Methods is relatively simple. By comparing the headspace from the MCF flask against that of the ordinary starch (from which the MCF was made) other effects tend to cancel and the effect found is due to the special nature of the MCF starch. Factors needed to convert GC peak areas to headspace concentration or partial pressure terms also cancel. The 30 min period allowed was found to be sufficient for the equilibrium to be produced. No significant changes were noted over the further 1–2 h needed to carry out the sampling (three for each flask). The mean for the standard deviations of the combined data in Table 1 was 11% of the ratios found.

Headspace Partial Pressure Ratios Found. Table 1 lists the ratio of the resulting headspace partial pressure (p) above MCF starch to that (p^0) above ordinary starch. It can be seen that the very volatile compound dimethyl sulfide showed little sorption by the MCF starch. Hydrocarbons, even moderately high boiling ones, such as decane and the terpene limonene, also showed little sorption. The partial pressure p of the C5 compound, 3-pentanone, in the MCF headspace was reduced to $^{7/100}$ of that in the ordinary starch headspace. That of hexanal was reduced to $^{3/100}$, that of 2,5-dimethylpyrazine reduced to $^{8/1000}$, and that of 2-ethyl-3-methylpyrazine reduced to $^{7/1000}$. It can be seen that the volatility and polarity of the compounds have a significant effect on the p/p^0 ratio. The reason for the greater sorption of the polar compounds may be the result of hydrogen bonding or dipole–dipole interaction occurring in the smaller micropores. The degree of reduction in partial pressure seems to show similarities to the compound's relative solubility in water. Hydro-

carbons such as decane and limonene are the least water soluble of the compounds in Table 1. Pyrazines and pyridines are the most water soluble and are known to participate in forming strong hydrogen bonds (Kasende and Zeegers-Huyskens, 1984).

Capacity of MCF Starch. Samples were examined with different proportions of 2-octanone to the starch beads. It was found that the optimum ratio for 2-octanone was 5.0 μ L/500 mg of MCF starch or ~1%. Using a load of 50 μ L/500 mg or ~10% showed only a factor of 2 reduction in partial pressure. This may be related to the available effective pore volume of the MCF starch, which showed 0.057 mL/g for micropores in the range of 5–14 Å (G. M. Glenn, unpublished results, 1995).

Release of Sorbed Compounds by Water. A major portion of each compound sorbed on MCF starch was readily displaced by water. With compounds having a low water solubility (e.g., 2-octanone), their headspace partial pressure (p) above the 0.50 g of MCF starch was largely (~>50%) restored, compared to that of the reference flask, within 30 min after the addition of 2 mL of water at room temperature (22 °C). Although they were released from the MCF starch with water addition, compounds that are quite water soluble showed a lower headspace partial pressure than the dry reference flask because of the lowering of p by solution effects according to Henry's law. A similar solution effect on p was observed on addition of water to the reference flask containing ordinary starch. Although a major portion of p was restored with water, it was never complete, which indicates that a percentage of the compound sorbed into the MCF starch is bound tightly enough that it is not displaced easily by water. This more tightly bound portion may be held in a small fraction of pores which are optimum in size for that molecule.

Comparison with Other Methods of Encapsulation. Numerous previous studies have been carried out with the use of starch for encapsulation or sorption of flavor and other organic compounds, which have been reviewed (Goubet et al., 1998; Godshall and Solms, 1992). These have included studies with ordinary starch (Hau et al., 1996) and also with modified starches. The processes involved are generally quite different from that used for MCF starch. Starch (or hydrolyzed starch) has often been used with spray-drying or extrusion methods to form a barrier around droplets of the emulsified flavor compound (Reineccius, 1989; Risch and Reineccius, 1988). Studies have also been carried out on starch inclusion complexes with organic compounds [cf. Rutschmann and Solms (1990)] using 1% starch solutions in water.

Spray-drying, extrusion, and formation of inclusion complexes generally require fairly vigorous conditions with a temperature of 100 °C or more, and they have been shown to be suitable for many stable flavor compounds. However, there are a number of potent important flavor compounds [e.g., (Z)-3-hexenal, 2-acetyl-4-hydroxy-2-pyrroline, and 2-acetyl-1-pyrroline] that are unlikely to survive such conditions. The MCF starch has the advantage that the sorption of the flavor compound can occur at relatively mild conditions at room temperatures.

Cyclodextrins are another related carbohydrate material that have been explored for use for flavor encapsulation. The cavity sizes in cyclodextrins are relatively fixed, for example, α - = 5.7, β - = 7.8, and γ - = 9.5 Å, respectively. These materials hold the sorbed molecules

tightly, and even though cyclodextrins have some ideal properties as carriers for flavor compounds, they do not release the encapsulated compounds very readily (Reineccius and Risch, 1986).

Although the size range of the micropores in MCF starch were determined, their exact nature is not clear. Rutschmann and Solms (1990) from X-ray diffraction studies have described organic inclusion compounds of starch as involving complexing of the organic compounds in the helical segments of amylose molecules (6–8 glucose units per helical turn). The main portion of cavities involved with the sorption in MCF starch is unlikely to be of this type and likely to be somewhat larger where the organic molecules are not bound so tightly. The dimensions appear to be confining enough, however, for hydrogen bonding effects to be important.

Comparison to Charcoal and Other Adsorbents. Some of the experiments were repeated with two other well-known sorbents, activated granular charcoal and the GC sorbent Tenax. These experiments were carried out in essentially the same way as used with the MCF starch, using 5.0 μL of compound to 500 mg of charcoal or Tenax. The flask used for comparison was empty except for the 5.0 μL of the compound. With both charcoal and Tenax the sorption factor was much greater, both showing headspace p/p^0 ratios of $<1/5000$ for 2-octanone, decane, and 3,5-dimethylpyridine.

Although less efficient, the mechanism of sorption with MCF starch appears to be similar to that which occurs with charcoal and Tenax. Whereas compounds sorbed on charcoal or Tenax are not readily displaced by water, they are usually displaced readily by solvent.

Activity and Reactivation of MCF Starch. Sorbents of the charcoal and Tenax type gradually lose their activity when exposed to laboratory atmosphere and need to be eventually regenerated, usually by heating. This was also found to be true with MCF starch. Samples of MCF starch beads, stored in plastic containers, lost much of their activity on storage for some months. This may be due to the sorption of the slowly released trace volatiles from the plastic or from atmospheric contaminants when the container was occasionally opened. It was found that this activity could be largely restored by heating the MCF starch at 100–110 $^{\circ}\text{C}$ for a few hours. No study was made on the effect of different moisture levels on the degree of adsorption.

Other Porous Starch Products. Popcorn is a product that consists principally of starch and has a porous structure. Experiments were carried out using freshly popped corn with 2-octanone again using essentially the same procedure as used for the MCF starch. However, no significant lowering of headspace partial pressure was found with popcorn. It is quite possible that the pore structure in popcorn is sealed, whereas Glenn and Irving (1995) have shown, using

scanning electron microscopy, that (at least for the larger pores) the MCF starch had an open pore structure.

Comparison between Wheat and Corn Starch MCF. No thorough comparison was made between the MCF forms made from wheat and corn starches, but the few experiments that were made showed that they behaved in essentially the same way. Some early experiments were made with corn starch MCF, but the data in Table 1 were determined with the wheat starch MCF.

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