Functionalized Flavors, Part II

Technology and methods for supporting controlled release, thermal resistance, flavor enhancement and off-flavor masking

Mike Porzio, Flavor Delivery Systems

The effective marriage of flavors with functionalized carriers will continue to become more important in food, nutrition and personal care systems; the flavorist who can obtain this added benefit for their flavors will have a decided advantage over their competitors.

Functionalized flavors are flavor systems in which the carriers or other delivery vehicles retain, enhance, amplify, release or protect flavor (character) until consumed in products. In many cases the carrier or delivery system becomes of equal or greater importance relative to the flavor. As technical sophistication regarding these functional delivery agents increases, their use becomes more important. An earlier discussion of functionalized flavors focused on some unique carrier systems and flavor chemicals.[1]

This article will characterize several functionalized flavor systems in the context of solving specific product requirements. Increasingly, current market dynamics drive requests from food, nutrition and personal care clients for flavors with control release properties, thermal resistance in heated environments, additional oxidative stabilization in terpene-based and other essential oils, reduced costs, and masking of specific off-flavor notes.

Commercial encapsulation technologies are the starting point for flavor functionalization. There are a number of excellent reviews, technical publications and symposia reports available, but they supply only general descriptions about the use of these flavor delivery technologies.[2–10] Detailed information regarding subtle carrier interactions with flavor systems, critical phase manipulations and practical commercialization issues are relatively nonexistent because of their proprietary nature.

Generating a functionalized flavor-carrier product requires sophisticated knowledge of flavor chemical properties, flavor-carrier interactions, the limits of encapsulation technologies, and now the sub-cellular signaling mechanisms of taste and flavor perception. A broad range of complimentary expertise is necessary to develop and modify carriers to solve the specific functionality requirements in a flavor delivery system. Large flavor houses have an inherent advantage in this endeavor with their extensive staffs, process systems and skilled specialists. **F-1** is a general model outlining interactivity of technical functions employed in development of a functionalized delivery system. The diagram characterizes feedback loops and their interrelationships during a typical project. The flavorist can leverage a number of these technical disciplines utilizing his/her key agent: the encapsulation or flavor delivery expert. Using complimentary skills, the flavorist and delivery specialist can become an effective team in meeting customer requests.

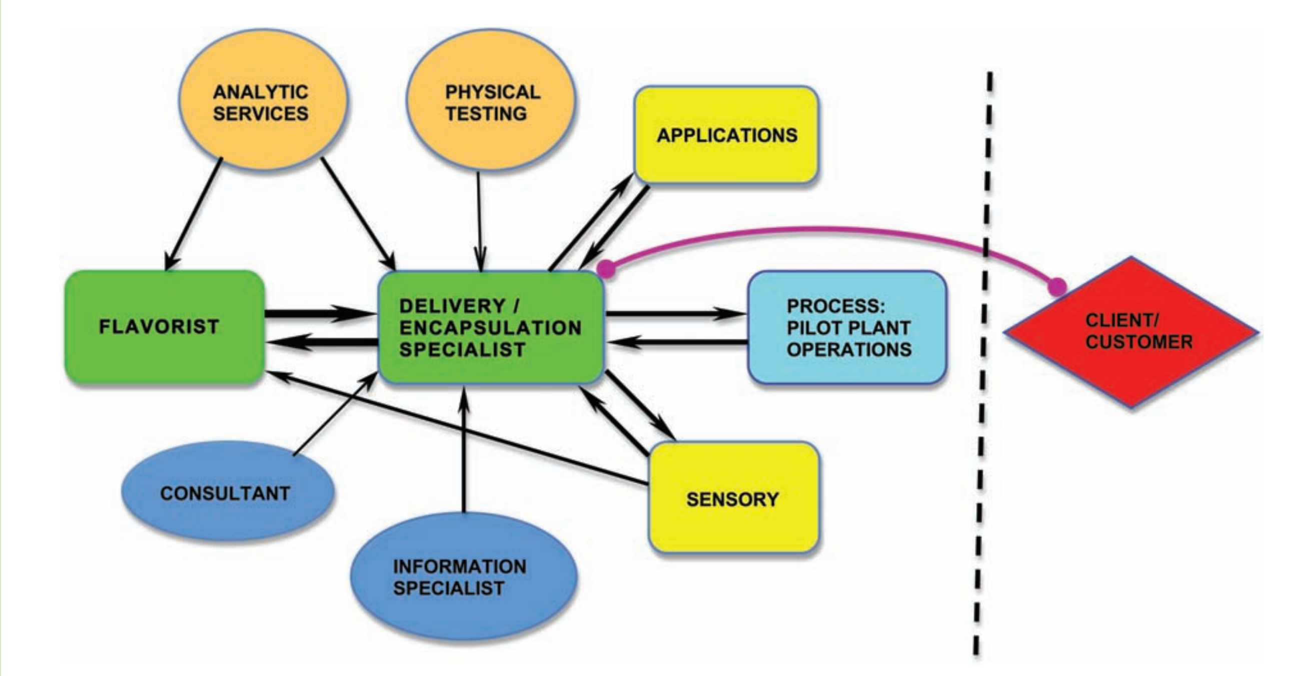
In starting any project the delivery expert goes through a mental checklist to determine key technical requirements for flavor performance in the product application and chooses an appropriate delivery technology. A paper by Ubbick provides a more formalized decision tree to identify the optimum, or most practical, delivery technology.[11] However a system is chosen, an incorrect choice of technology usually leads to project failure.

Flavor Encapsulation and Functional Flavors

The major commercial forms of encapsulated flavors include spray drying, spray chilling (lipid encapsulation) and melt extrusion. Other flavor encapsulation and delivery systems are lesser contributors and include complex coacervation, β-cyclodextrin complexation, liposomes, melt injection and microemulsions. While the three major systems yield encapsulated flavors as solid powders, they exhibit limited or no release functionality to provide a basis for a functional flavor. Since spray dried, melt extruded, and melt injected encapsulating matrices are generated from water-soluble carbohydrates into a glassy solid, exposure to heat and moisture will result in a rapid release of any encapsulated flavor.

Functionalized flavor systems have been developed and commercialized over the past decade by a number of flavor houses for specific flavor needs. Four examples of these functionalized flavors are discussed in terms of the particular flavor system and delivery requirements. They include thermal stable (bake-proof) flavors, spray dried fruit flavors for drink mixes, reaction fried flavors by extrusion, and flavor modulation, i.e. amplification of the sensory flavor impact.

A general model outlining interactivity of technical functions employed in development of a functionalized delivery system **F-1**



Bake-proof Flavors

Flavors consisting of aromatic, low molecular weight volatile constituents are rapidly lost upon heating. Most standard encapsulated flavor systems do not provide any protection during industrial processing or in consumer applications. The logical approach to thermal stabilization is to make use of the unique reversible thermal transitions of the methylcellulose polymers.[12] Several approaches are found in reports describing the use of cellulose gums for this purpose. US Patent 3,567,650 by Brynko teaches a "simple" coacervation encapsulation process with methylcellulose and uses dextrans to induce the phasing out of the polymer to form lemon oil capsules.[13] This patent also teaches further chemical cross-linking of the methylcellulose polymer phase to expedite stabilization and collection of the oil-filled capsules, but no mention was made of the encapsulated lemon oil properties relating to heat and oxidative stability or release in food systems.

Another disclosure by Porzio and Madsen employed methylcellulose polymers in an alternate "simple" coacervation process.[14] Sodium hexametaphosphate was used to initiate the desired phase inversion of the methylcellulose to form a polymer membrane around a flavor oil droplet. In this procedure the resulting coated flavor oil droplets were not cross-linked, but used *in situ*. Maltodextrins were added to the aqueous system, dissolved in the flavor-carrier dispersion and immediately spray dried. This patent application was abandoned, however, due to the extreme difficulty in controlling the kinetics of the methylcellulose phase deposition and membrane coating when scaling up the laboratory procedure for commercial production.

Since methylcelluloses do not contain acidic or basic groups, the polymer is not functional for use in a complex coacervation process. Also, it is known that any coacervation encapsulation technology (simple or complex) is limited to hydrophobic flavor oils. Flavors with surface-active components or water-soluble components interfere with the oil-polymer interfacial wetting dynamics and prevent effective polymer film formation.

Controlling the reversible phase behavior of the methylcellulose (and hydroxypropylmethyl cellulose) polymers with both W/S and O/S flavors to generate the desired thermal control and release properties has been achieved. A simple, easily scaled commercial process is available utilizing selected methylcellulose polymer forms and manipulating polymer-polymer and flavor-polymer interactions.

This functionalized flavor system exhibits thermal stabilization and controlled release properties and is well suited to drink, soup, cake and baking mixes, as well as for use in half products as in the manufacturing of snacks, cereals and instant food products. The flavor is retained in the polymer system when heated, but is then released upon cooling.

Fruit Drink Powders

Fruit flavored drink mixes with a distinct fresh top note rely on spray dried fruit flavors, which are subsequently blended with sugars, acids and maltodextrin bulking components by the manufacturer to generate the mixes. Most compounded fruit flavors consist of water-soluble components and preferably contain significant acetaldehyde (FEMA# 2003) levels in the top note for the desired fresh sensory character.

A standard formulary approach incorporates acetaldehyde as part of the W/S compounded flavor. There are two main commercial acetaldehydes generally available,

Flavor ingredient properties of acetaldehyde (FEMA# 2003)			T-1
Form:		**Pure (99%)**	**50% in ETOH**
Stored refrigerated	% CH3CHO	95–99%	50%
w/Solvent	% CH3CHO actual	-	30–35%
	% Solvent actual	-	20–30%
	% Acetal form	-	25–35%
	% Trimer (paraldehyde)	(est. 1–5%)†	5–10%†
Stored in freezer	% Quadramer (metaldehyde)	(trace–3%)*	(est. 1–3%)
Flash point (closed cup)		-38°C	-30°C
Flammable limits (%)		4 to 60	

† Depending upon storage temperature and length of storage
* Metaldehyde forms at temperatures < 0°C; reverts to acetaldehyde > 80°C

but they contain nonequivalent characteristics. **T-1** gives a comparison of pure and 50% ETOH acetaldehyde materials. Either system will likely result in significantly reduced acetaldehyde levels due to loss by volatilization during spray drying. Formation of a trimer and reaction with alcoholic co-solvent to form the diethyl acetal (FEMA# 2002) contributes to diminution of free aldehyde in the alcohol-acetaldehyde solution.

Adjusting flavor character by increasing top note levels to compensate for losses can sometimes unbalance the major flavor character. Considering the end goal of consistently delivering the fresh character to the spray dried fruit powder, one alternative approach is to prepare a separate spray dried acetaldehyde ingredient. With the 99% acetaldehyde dissolved in a high solids maltodextrin-corn syrup carrier solution, a spray dried, encapsulated acetaldehyde can be produced as glassy state powder with a glass transition temperature (T_g) > 35°C and with acetaldehyde loads in the range of 4–8% (w/w). When employing this strategy safety issues involving aldehyde vapor build up, and the potential for ignition and explosion must be carefully considered, and extreme care and extensive safety practices observed. After spray drying the balance of the fruit flavor formula minus acetaldehyde, the powdered acetaldehyde is post-blended with bulk flavor component to accurately yield acetaldehyde at the desired final formulation level.

A more sophisticated approach builds on the separately spray dried-reblended strategy, but without the same safety issues. The flavor (2-di((1'-ethoxy)ethoxy) propane) (FEMA# 3534) is a polyacetal consisting of two acetaldehyde molecules, one propylene glycol and two ethanol molecules. This precursor aldehyde rapidly releases the free acetaldehyde by hydrolysis in weakly acidic aqueous solutions. To prevent undesired hydrolysis during the standard spray drying process with the holding of the bulk flavor solutions, acidic carriers such as octenyl succinate (OSAN) starches or gum arabic must be avoided.
A preferred carrier solution is made up with maltodextrin-corn syrup solids and is preneutralized or buffered to pH 7.0–7.5 before addition of the polyacetal and spray drying. This approach markedly reduces or eliminates any free acetaldehyde release. The spray dried polyacetal powder is added back to the spray dried flavor base as noted before. When the fruit drink powder is stirred into water and dissolved, the solubilized fruit acids of the mix will generate a solution pH of 3.0–4.0, releasing the top note aldehyde to supply the desired fresh note character.

A more technically astute solution utilizes melt extrusion technology. Fulger's patents teach a melt extrusion process which injects acetaldehyde under pressure into the molten carrier followed by pressure cooling of the exiting carbohydrate melt.[15] The matrix retains the acetaldehyde in excellent yield and in the desired glassy solid state. Scanning electron microscope (SEM) photographs of atmospheric cooled versus pressure cooled melt extruded acetaldehyde products clearly verify the key functionality. The pressure cooled matrix exhibits a continuous solid surface, while the atmospheric cooled product shows pores and holes resulting from gaseous acetaldehyde flashing off before the melt has cooled sufficiently to solidify.

There are engineering issues and specific process systems necessary to cool a molten extrudate in a continuous operation under pressure. The system would require a manifold delivery unit to deliver the melt for static cooling in pipes or chambers. A very similar system was described for the manufacture of the novelty candy *Pop Rocks*, which contains significant levels of gaseous CO_2. A very readable history of the manufacturing issues required to prepare commercial quantities of this novelty candy is found in Rudolph's published account.[16]

Extrusion Fried Flavors

Flavorists who specialize in developing reaction flavors generally use water, oil or o/w emulsions as the reaction media. Generation of specific flavors requires selection of the proper flavor precursors, solvent and controlling the kinetics of formation of the desired flavor systems.

Cooking extruders for processing of farinaceous materials do not retain significant browned flavors due to the steam flashing of exiting melt moisture. For cereals and snacks, flavors are generated by toasting in ovens or enrobing the dry product with flavor containing syrups, emulsions or dry blends.

Recently melt extrusion has been adapted to the continuous production of savory meat flavors by industrial suppliers. Specific amino acids and reducing sugars are combined and added to a carrier feed and extruded continuously to produce chicken, pork and beef reaction flavors. The low cost of processing, excellent flavor character, recovery of the reaction flavor in a solid glassy state (that can be milled, sieved and packaged in a continuous production line) gives this reaction flavor manufacturing system specific economic advantages.

Reaction flavors associated with the frying process are more difficult to generate by an extrusion process. Normally, fried notes are developed by addition of the food tissue in frying oils heated to ~350–375°F. The complex flavor chemistry of frying yields extremely desirable flavors, especially when employing potato or onion tissue. Using the extruder and attempting to deliver the oil into the feed port immediately unbalances the melt flow dynamics in the extruder. Oils (or the melted fats) act as slip agents and reduce the viscosity drag of the protein-carbohydrate base and heat transfer. Addition of more than ~5% oil leads to unbalanced melt flow and separation of the oil from the melt.

Pitchon claimed a process for extrusion frying in a conventional extruder.[17] The extrusion of a farinaceous material starts by cooking the protein-carbohydrate base, followed by injecting preheated oil into the melt zone. This process does not yield a rich fried flavor, but rather more correctly cooked flavors.

A more practical route to extruded fried flavors makes use of selected flavor precursors, specifically treated ingredients and the applicable commercial extruder system to generate high impact fried flavors. The deep, freshly fried note is generated as a solid which can be used as a flavor additive in snacks and toppings.

Flavor Modulation

Amplification of flavor and taste can be achieved by formulating a carrier-encapsulation system that utilizes specific enhancing agents as part of the formula. A general discussion of the flavor modulation technology was presented in a recent article.[18] The carrier's complex formula involves both specific adjuvants, enhancing agents and carriers designed to elicit specific physiological responses. In this system, the flavor, flavor solvent, multiple enhancing agents, adjuvants, proteins, sugars, salts and surfactants are meticulously formulated and evaluated by sensory panels. A series of controlled formula and phase changes are executed and the optimized formula spray dried under very controlled process conditions.

This modulation system can be utilized in four main areas: ingredient replacement, flavor enhancement to allow reduced flavor levels, combined compatible flavor enhancement with off-flavor masking, and flavor masking. The first use developed with this technology involved formulating ingredient replacers with all the sensory characteristics of the original ingredient, but with significant reduction of cost in usage. Among ingredients replaced were aged cheeses, sodium chloride, fruit powders and other dairy systems.

By combining several modulating flavor systems in a mixture such as a seasoning blend, significant additional cost savings are possible. An example of this amplification response was illustrated in the formulation of a cheese seasoning for topical application on snacks. A seasoning formula was prepared with and without one key adjuvant agent at a level of 15 parts per trillion in the formula as consumed. A trained sensory panel was able to distinguish between the two samples and preferred the "with adjuvant" sample as having slightly increased cheese character and total flavor.

Another application of the modulating system involves producing spray dried flavors. By amplifying the sensory response to the flavor, use levels are reduced while obtaining equivalency in sensory properties. In many cases a reduction of 50–90% in flavor use is possible.

The technology can be extended to masking of many specific off notes characterized as bitter, chemical, beany, earthy, and metallic, among others. The masking system is based upon amplification of the sensory response to the specific masking agent in the modulation carrier. Masking agents are likewise reduced in use and are effective at the parts per billion range of masker as a surface dusting agent on an as-consumed basis.

As noted, the flavor modulation system has been commercialized in development of dairy and fruit ingredient replacers, for heat amplification, masking of bitter off notes from caffeine and KCl, and amplifying the Na^+ signal for low-salt seasonings and dry mixes. The technology is applicable only in dry flavoring systems. Heat and moisture can modify the delicately balanced carrier phases with a resulting loss of functionality. However, the ability to reduce flavor levels by 50–90% in product applications gives a strong economic incentive advantage in their development. Flavor modulation of specific fruit, dairy or cheese flavors can only be applied by reducing use levels. Otherwise the effect with overuse of the modulated flavor leads to sensory pacification or "flavor fatigue."

This effective marriage of flavors with functionalized carriers will continue to become more important in food, nutrition and personal care systems. The flavorist who can obtain this added benefit for their flavors will have a decided advantage over their competitors.

Address correspondence to Mike Porzio, Flavor Delivery Systems, PO Box 382, Hunt Valley, MD 21030; mporzio9@comcast.net.

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