Stability of vitamins in pelleting

BY N.E. WARD, PHD, MSC

REVIEWED AND EDITED BY CHARLES STARK, ADAM FAHRENHOLZ, AND CASSANDRA JONES

Pelleting of animal feeds has been practiced for decades. During the pelleting process, an increased processing temperature is associated with the production of more tonnes of feed per hour with improved pellet durability. If conditions are harsh enough, however, reduced starch (Brown, 1996) and protein (Batterham, *et al.*, 1993) utilization can occur.

In addition, the moisture, heat, friction and shear of pelleting can compromise the integrity of added vitamins (Jones, 1986; Gadient, 1986) and enzymes (Nunes, 1993; Eeckhout, 1999). Taken that the various feed additives are inherently vulnerable to heat and moisture, this is not a minor concern. Thus, it's important to understand the conditions that might decrease the efficacy of enzymes and vitamins in a processed feed.

Vitamins

The task facing vitamin manufacturers is to produce vitamins so that losses during storage or feed processing are minimized or eliminated—while maintaining maximum bioavailability and mixing characteristics in a cost-effective manner. The stability of commercial vitamin products is generally good, and is superior to vitamins occurring naturally in feedstuffs (Kurnick, *et al.*, 1978).

As new sources of vitamins are introduced, questions should exist about their manufacture and individual stability characteristics. Not all sources of a particular vitamin are necessarily stabilized in the same manner, and in some cases proprietary or patented technology is utilized. Thus, differences can exist in stability, not only by source, but also with formulation changes from the same supplier. For these reasons, historical data must be closely scrutinized.

Vitamin stability characteristics

Inherent differences exist in the stability of unformulated vitamins (i.e., non-commercial forms; Baker, 1995). Thus, while heat may be especially destructive to vitamin A, it has little consequence on niacin (**Table 16-1**). Vitamins for use in feeds and foods are formulated to counter anticipated stresses, and formulations are intended to act as a buffer between the vitamin and the destructive component.

Along with the unique chemical structure and characteristics of each vitamin, the anticipated stress dictates the type of stabilization or formulation needed. For example, vitamin A exists with four double bonds and one hydroxyl group (Adams, 1978). This chemistry predisposes this vitamin to oxidation, thus vitamin A esters (actetate, palmitate, propionate) help avoid oxidative damage. Additional formulating and beadlet formation provides heightened protection against moisture and exposure to light.

The antioxidant capabilities of the tocopherols, through the free phenolic hydroxy group, compromise the stability of vitamin E (in the alcohol form). Esterification with acetic acid eliminates its antioxidative nature, thereby improving stability. Vitamin K (menadione) continues to be the most unstable commercial vitamin due to its structure, although modifications have improved stability.

Thiamin and folic acid are prone to bind with the carbonyl group of reducing sugars through the

Maillard reaction (Baker, 1995), and higher pelleting temperatures increase this occurrence. On the other hand, in crystalline form with no special protection, calcium pantothenate, niacin and niacinamide (nicotinamide) exhibit good stability for pelleting.

Table 16-1. Factors affecting inherent vitamin stability. O =stable, X = sensitive, XX = very sensitive.						
Vitamin	Heat	O$_2$	H$_2$O	Light	Acid	Alkali
A	XX	XX	X	XX	X	O
D$_3$	X	XX	X	X	X	O
E	X	O	X	X	O	X
K	X	X	XX	O	XX	O
Thiamin	X	X	XX	O	O	XX
Riboflavin	O	O	X	XX	O	O
Pyridoxine	XX	O	X	X	X	O
B$_{12}$	XX	X	X	X	O	O
Niacin	O	O	O	O	O	O
Folic Acid	XX	O	XX	XX	XX	O
Biotin	X	O	O	X	O	O
C	O	XX	XX	O	O	X

Formulation of vitamins

Heat, moisture and conditioning time can affect the stability of most vitamins during pelleting. By simply acting as a solvent, moisture can favor harmful chemical reactions. Moisture can also soften the coating of some beadlet and spray-dried forms, thus exposing the vitamin to oxygen and other destructive chemical components such as trace minerals (Gadient, 1986).

Thus, the basic chemical forms of vitamins are further processed and formulated to avoid some of the most obvious stresses and to counter some inherent weaknesses (see **Table 16-2**). There are several basic formulation techniques for the manufacture of feed-grade vitamins:
• Chemical modification;
• Beadlet preparation in a cold starch mist;
• Spray-drying in a hot air current;
• Adsorbents onto a stable dry carrier;
• Agglomeration; and
• Sieving to select appropriate particle sizes.

Some vitamins are innately more stable during pelleting and require only minimal formulation,

while other vitamins may need substantial formulation changes to attain reasonably good stability. With a better understanding of the individual formulations, one can sometimes avoid or modify conditions that might be especially damaging, or modify addition rates according to expected losses. More than one form of a vitamin can sometimes exist, and depending upon the intended use, one may be chosen over the other.

Not all formulation types confer equal stability characteristics to a vitamin. In one recent experiment, as much as 20% difference existed across four different sources of commercial vitamin A pelleted at 90˚C (DSM internal documentation,VFP9964).

Table 16-2. Common commercial vitamin forms and their stability.		
Vitamin	Rationale	Formulation
A	Ester in cross-linked beadlet	Stability
D$_3$	Spray-dry	Stability, Uniform distribution
E	Acetate ester granular or spray-dry	Stability, Flow, Reduced dust
K	Crystalline powder	Flow, Handling
Thiamin	Coarse granular	Stability
Riboflavin	Spray-dry granular	Stability, Flow, Handling
Pyridoxine	Fine granular crystalline	Stability, Mixing with Carrier
Vitamin B$_{12}$	Crystalline	Distribution with carrier
Niacin	Crystalline	Flow Reduced Dust
Biotin	Spray-dry	Distribution, Handling
Folic Acid	Spray-dry	Flow, Stability, Mixing
C	Ethyl cellulose coated	Stability, Biopotency

Chemical modification

A chemical modification can enhance stability without adversely affecting the vitamin's bioavailability. The crystalline form of vitamin C is easily destroyed by moisture and pelleting, and exposure to trace minerals such as copper and iron potentiates losses. The esterification of the two-carbon atom of L-ascorbic acid with phosphate protects L-ascorbic acid from oxidation (Grant, *et al.*, 1989).

One commercial form of vitamin C stabilized in this manner consists of a mixture of tri-, di- and monophosphate esters of L-ascorbic acid, and was designed specifically for extruded feeds, or feeds pelleted at high temperatures (Roche Animal Nutrition, 1991).

Plants and some oils contain several tocopherols with naturally occurring vitamin E activity. However, as an alcohol, it is an effective antioxidant. Substantial losses can occur during processing, especially during storage when exposed to oxygen (De Ritter, 1976). Trace minerals can exacerbate losses (Adams, 1973; Dove and Ewan, 1986). The esterification to alpha-tocopheryl acetate stabilizes vitamin E for most pelleting conditions. This form is widely used in the feed industry because the acetate moiety eliminates its reactive antioxidative character (Adams, 1978).

Menadione is a chemically-unstable compound, and losses can be substantial over the weeks following pelleting. Although various formulations (including spray-dried) have been tested to improve its stability, the menadione di-methyl pyrimidinol bisulfite (MPB) and menadione nicotinamide bisulfite (MNB) appear to be the most stable forms (Huyghebaert, 1991). The combination of menadione and nicotinamide (MNB) provides the greatest advantage for pelleting (DSM internal documentation).

Thiamin mononitrate is preferred in feeds (Adams, 1978). Thiamin hydrochloride is more soluble and is preferred for liquid preparations, but it is prone to greater losses during pelleting. D-pantothenic acid is the preferred form (the l-isomer has no vitamin activity), but due to its unstable and hygroscopic

nature, is utilized as the calcium salt as the d-isomer since the dl-pantothenate is hygropscopic with poor handling characteristics. And while the spray-dried granular version of riboflavin is preferred for feeds to avoid excessive dust and accumulation onto mixing equipment, the use of crystalline riboflavin-5-phosphate sodium is far more suitable for liquid applications due to a much greater solubility.

Coating or encapsulation technology

Coatings (e.g., carbohydrate, protein, ethyl cellulose) or encapsulation gives vitamins such as vitamin A and D_3 greater protection against moisture, heat and pressure during pelleting (De Ritter, 1976). Commercial forms of vitamins A and D, as well as some commercial carotenoids, exist in the matrix of a cross-linked beadlet generally composed of gelatin, sugar, gum, starch or some similar type of hydrocolloid. The inclusion of antioxidants such as ethoxyquin, BHA, BHT or tocopherols offers additional protection against oxidizing agents. The smooth spherical shape of the beadlets is usually coated with starch to prevent segregation in feeds.

Today's beadlets commonly include cross-linked gelatin. In early literature this technology was referred to as "hardening" because it physically hardened the beadlet through the cross-linked gelatin proteins. This beadlet minimizes contact with moisture and trace minerals because it is more dense and impervious to water. It disintegrates in the acidic stomach environment in the presence of enzymes, thus bioavailability is not an issue. This process results in minimal losses when pelleting at 85-95°C. The cross-linked beadlet also reduces the potentially-negative effect of shear or pressure during pelleting (Gadient, 1986).

In an early study, vitamin A in a beadlet cross-linked with gelatin was compared to a non-cross-linked vitamin A beadlet. Both were exposed to an aggressive trace mineral premix with choline chloride. After a 30-day period, the cross-linked vitamin A lost 6% activity while the non-cross-linked vitamin A lost 35% of its original activity (DSM internal documentation). The spray-dried

version of vitamin A is understandably less stable than either of the beadlet forms.

However, not all encapsulated products experience protection against losses during feed processing (Gadient and Fenster, 1992). While encapsulated ascorbic acid products are excellent sources of vitamin C (Hilton, *et al.*, 1977), only marginal improvements exist when pelleted in feeds. On the other hand, an ethylcellulose coating for vitamin C has successfully enhanced its stability characteristics, but not to the same degree as with the phosphorylated vitamin C.

Spray-dried formulations

Spray-dried formulations of vitamins usually provide an improvement in the stability during pelleting. The process of spray-drying includes a mixture of the vitamin, antioxidant, gelatin, maltodextrin and water that is sprayed into an environment of hot air. A non-starch emulsion is used to produce a granulated product with a lower solubility in water. This process provides some "embedding" of the vitamin within the particle, although it differs from a coated beadlet (**Figure 16-1**). Spray-drying reduces the electrostatic nature of some vitamins, and increases the particles per unit.

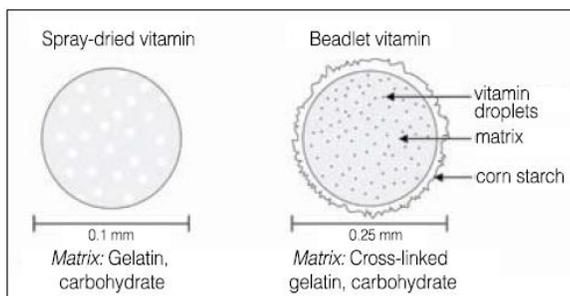**Figure 16-1.** Comparison of beadlet and spray-dried formation.

Figure 16-2 shows the results of a study with two forms of folic acid (spray-dried and conventional crystalline). The spray-dried formulation of vitamin E is generally a little more pelleting-stable than is vitamin E adsorbate. In one internal study, the retention of the spray-dried form with the gelatin coating was 95%, versus 88% for the adsorbate at 90°C pelleting temperature.

Figure 16-2. Pelleting retention of crystalline and spray-dried formulation of folic acid (VFP22043).
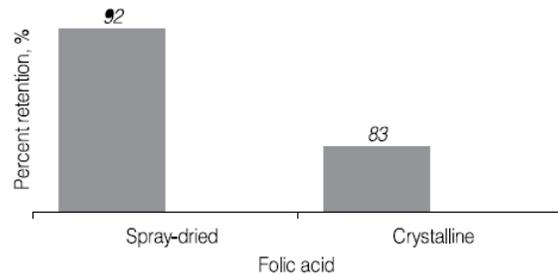
Vitamins such as vitamin E (as the acetate), vitamin D, riboflavin, biotin, pantothenic acid, pyridoxine, folic acid and vitamin C (as the phosphate ester) are usually offered in spray-dried or spray-granulated formulation.

Others

Niacin, niacinamide, menadione, calcium pantothenate and thiamine generally exist in the crystalline form. Niacin or niacinamide in this form has high purity (99%) and excellent pelleting stability. In spite of niacinamide's very high solubility, its stability does not differ from that of niacin.

As a diluted formulation, vitamin B_{12} (cyanocobalamin) is relatively stable to pelleting, but is sensitive to oxidizing and reducing agents. Ascorbic acid, niacinamide and breakdown products of thiamin are known to accelerate its decomposition (Kurnick, *et al.*, 1978). Vitamin B_{12} should be diluted for mixing.

Vitamin stability

At one time (Gadient, 1986), the primary vitamins of concern for stability were vitamins A and D, menadione, thiamin and vitamin C. Today, progress has been made such that we could probably remove vitamins A, D and C from that list. Efforts to improve stability of formulated vitamins in pelleted feeds have been successful, especially for temperatures of 75°C or less, when losses certainly would be minimal.

In a recent field study, the stability of vitamin A, vitamin E adsorbate, riboflavin, thiamin and folic acid was determined when the feed was conditioned for three minutes at 96-99°C, and in a cooker for five seconds at 115°C. Losses of approximately 10% occurred with vitamin A, riboflavin and folic acid. While no loss occurred with thiamin, about 25% of the vitamin E was lost. Thus, under relatively-harsh conditions, stabilities were generally good overall.

Some nutritionists make adjustments in their formulations to account for anticipated losses (Perry, 1978), as reflected in commercial averages (Ward, 1993). Gadient and Fenster (1992) reported a loss of about 20-30% of most vitamins when stored three months at 35°C after being pelleted at 90°C. Once the vitamins go through pelleting and exposure to moisture, the protective coatings are often damaged such that contact with trace elements and moisture becomes more possible. Losses in vitamins due to various storage conditions have been suggested (Kurnick, *et al.*, 1978; Anonymous, 1991; Albers, 1996; Coelho, 1996). At room temperature for 8 weeks after pelleting, thiamin, menadione, pantothenic acid, folic acid and vitamin B_{12} appeared most prone to losses (Albers, 1996).

It is reasonable to assume that higher pelleting temperatures result in higher losses post-pelleting, since more of the protective coating is likely destroyed. While the majority of poultry and swine feeds is fed within days after pelleting, bagged pelleted feeds might be stored for several weeks or months before being fed. Considerations must be made for the pelleting temperature and the time lag between pelleting and feeding, since a greater loss in potency occurs with prolonged storage. Unless the conditions are known, it is difficult to predict losses.

References

Adams, C.R., 1973. Effect of processing on the nutritional value of feeds. National Academy of Sciences, Washington, DC, USA.

Adams, C.R., 1978. Vitamin product forms for animal feeds. Hoffmann-La Roche vitamin update, Arkansas Nutrition Conference, Hot Springs, Arkansas, USA.

Albers, N., 1996. The influence of the production process and the composition of the mixture on vitamin stability. *Feed Compounder*, April.

Angel, R.A. and Ward, N.E., 2005. Comparison of phytases after being pelleted. Unreported.

Anonymous, 1991. Stability of vitamin products. VITEC Ser. Tech. Leaf., Ref. G3 2/1. Hoffmann-La Roche Ltd., Basel, Switzerland.

Baker, D.H., 1995. Vitamin bioavailability. Bioavailability of nutrients for animals: Amino acids, minerals and vitamins. Academic Press Inc., New York, New York, USA.

Barendse, R.C.M., 1995. Technological aspects of enzyme usage. Second European Symposium on Feed Enzymes. Noordwijkerhout, Netherlands, 178.

Batterham, E.S., Anderson L.M. and Baigent, D.R., 1993. Utilization of ileal digestible amino acids by growing pigs: Tryptophan. *Brit J Nutr* 71:345.

Beardsworth, P., 2004. Technology preserves phytase activity. *Feed Mix* 12(2).

Bedford, M.R., Pack M. and Wyatt, C.L., 1997. Relevance of in-feed analysis of enzyme activity for prediction of bird performance in wheat-based diets. *Poultry Sci* 76(1):39.

Bedford, M.R., 2000. Exogenous enzymes in monogastric nutrition—their current value and future benefits. *Anim Feed Sci Tech* 86:1.

Behnke, K.C., 1998. Why pellet? Kansas State University/AFMA Pellet Conference, Manhattan, Kansas, USA.

Brown, I., 1966. Complex carbohydrates and resistant starch. *Nutr Rev* 54:S115.

Clemmensen, J., Westh, P. and Fuglsang, C.C., 1999. Phytase interaction with water. Unpublished.

Coelho, M., 1996. Stability of vitamins affected by feed processing. *Feedstuffs* July 29.

De Ritter, E., 1976. Stability characteristics of vitamins in processed foods. Food Tech

30:48.

Dove, C.R. and Ewan, R.C., 1986. Effect of diet composition on the stability of natural and supplemental vitamin E. *Swine Res Rep* AS-80-J. Iowa State University, Ames, Iowa, USA.

Eeckhout, I.M., 1999. Phytase quality suffers from steam pelleting and storage temperature. *Feed Tech* 4(2).

Engelen, A.J., van der Heeft, F.C., Randsdorp, P.H.G. and Somers, W.A.C., 2001. Determination of phytase activity in feed by a colorimetric enzymatic method: Collaborative inter-laboratory study. *J AOAC Intern* 84:629.

Froetschener, J., 2005. Current and future mill technology. Arkansas Nutrition Conference, Rogers, Arkansas, USA, 122-143.

Gadient, M., 1986. Effect of pelleting on nutritional quality of feeds. Maryland Feed Manufacturers, College Park, Maryland, USA.

Gadient, M. and Fenster, R., 1992. Vitamin stability in aquaculture feeds. *Fish Farmer* February.

Gadient, M. and Tritsch, J.C., 1995. Product formulations for enzymes used in animal nutrition. Second European Symposium on Feed Enzymes, Noordwijkerhout, Netherlands.

Garret, J.B., Kretz, K.A., O'Donoghue, E., Kerovuo, J., Kim, W., Barton, N.R., Hazlewood, G.P., Short, J.M., Robertson, D.E. and Gray, K.A., 2004. Enhancing the thermal tolerance and gastric performance of a microbial phytase for use as a phosphate-mobilizing monogastric-feed supplement. *Appl Environ Microbiol* 70:3041.

Grant, B.F., Seib, P.A., Liao, M. and Corpron, K.E., 1989. Poly-phosphorylated L-ascorbic acid: A stable form of vitamin C for aquaculture feeds. *J Wrld Aqua Soc* 20:143.

Harz, H.P. and Betz, R.J., 1999. Salt-stabilized enzyme preparations. US Patent 5,972,669.

Hilton, J.W., Cho, C.Y. and Slinger, S.J., 1977. Factors affecting the stability of supplemental ascorbic acid in practical trout diets. *J Fish Res Board Canada* 34:683.

Hooge, D.M., Steward, F.A. and McNaughton, J.L., 2000. Improved stabilities if vitamins A, D_3, E and riboflavin with tri-basic copper chloride (TBCC) compared to copper sulfate penta-hydrate in crumbled broiler starter feed. *Poultry Sci Abstr* No. 189, Montreal, Canada.

Huber, T. and Gadiet, M., 2002. Stability performance of feed additives in a long-time conditioned layer feed. VFP22043, DSM Nutritional Products, Inc., Basel, Switzerland.

Huyghebaert, A., 1991. Stability of vitamin K_3 in a mineral premix. *World Poultry* 7:71.

Jacobsen, K.T. and Jensen, P.E., 1995. Use of an enzyme containing granulate in a method for production of a pelletized fodder. US Patent 5,391,371.

Jones, E.T., 1986. Effect of pelleting on vitamin A assay levels of poultry feed. *Poultry Sci* 65:1421.

Kurnick, A.A., Hanold, F.J. and Stangeland, V.A., 1978. Problems in the use of feed ingredient vitamin values in formulating feeds. Georgia Nutrition Conference 107-136.

Lehmann, M., Pasamontes, L., Lassen, S.F. and Wyss, M., 2000. The consensus concept of thermostability engineering of proteins. *Biochim Biophys Acta* 1543:408.

McKinney, L.J. and Tetter, R.G., 2003. Caloric value of pelleting and the consequential creation of nutritional dead zones. *Poultry Sci* 82(1):109.

McNight, W.F., 1996. Use of NSP enzymes in swine and poultry nutrition. BASF Technical Symposium, Pacific Northwest Nutrition Conference, Seattle, Washington, USA.

Nunes, C.S., 1993. Evaluation of phytase resistance in swine diets to different pelleting temperatures. Enzymes in Animal Nutrition, Kartause Ittingen, Switzerland, 269.

Perry, S.C., 1978. Vitamin allowances for poultry and swine. Hoffmann-La Roche vitamin update, Arkansas Nutrition Conference, Hot Springs, Arkansas, USA.

Pickford, J.R., 1992. Effects of processing on the

stability of heat-labile nutrients in animal feeds. *Rec Adv Anim Nutr* 177-192.

Raastad, N. and Skrede, A., 2004. Feed pelleting temperature influences growth performance of broiler chickens.

Roche Animal Nutrition, 1991. Technical update: Stay-C stabilized vitamin C. RCD 8425/491. Hoffmann-LaRoche, Inc., Nutley, New Jersey, USA.

Schutte, J.B. and Pack, M., 1995. Sulfur amino acid requirement of broiler chicks from fourteen to thirty-eight days of age: Performance and carcass yield. *Poultry Sci* 74:480.

Silversides, F.G. and Bedford, M.R., 1999. Effect of pelleting temperature on the recovery and efficacy of a xylanase enzyme in wheat-based diets. *Poultry Sci* 78:1184.

Smith, A., 2005. Post-pelleting liquid application. Arkansas Nutrition Conference, Rogers, Arkansas, USA.

Thomas, M., van Zuilichem, D.J. and van der Poel, A.F.B., 1997. Physical quality of pelleted animal feed: Contribution of processes and its conditions. *Anim Feed Sci Tech* 64:73.

Ward, N.E., 1993. US commercial vitamin supplementation rates for broilers, turkeys and laying hens. *J Appl Poultry Res* 2:286.

Ward, N.E. and Wilson, J.W., 2001. Pelleting stability of Ronozyme P (CT) in commercial US feed mills. *Poultry Sci Abstr* No. 1968, Indianapolis, Indiana, USA.

Wyss, M., Brugger, R., Kroneberger, A., Remy, R., Fimbel, R., Oesterhelt, G., Lehman, M. and van Loon, A.P., 1999. Biochemical characterization of fungal phytases (myo-inositol hexa-kisphosphate phopshohydrolases) catalytic properties. *Appl Environ Microbiol* 65:367.

Wyss, M., 2005. Personal communication.

Dr. Nelson E. Ward is the Poultry, Technical Marketing & New Business Development Manager at DSM Nutritional Products, Inc. He received his M.S. and Ph.D from Clemson University.

This content was edited and reviewed by Dr. Charles Stark, Jim and Carol Brown Associate Professor of Feed Technology at Kansas State University, Dr. Adam Fahrenholz, Assistant Professor of Feed Milling at North Carolina State University, and Dr. Cassandra Jones, Assistant Professor of Feed Technology at Kansas State University.