

# Vitamin retention in extrusion cooking

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> Extrusion cooking (high-temperature short-time) represents a very efficient processing technology, which enables the manufacture of a wide variety of food and feed products on the basis of grain. Effects of extrusion cooking on nutritional quality are ambiguous. Positive influences can be seen in increasing digestibility or in the inactivation of undesirable substances. However, as far as vitamins are concerned, depending on production parameters, mainly destructive effects are reported. Depending on the particular vitamin, considerable degradation can occur, especially in products with high sensory appeal. This paper reviews the existing knowledge about vitamin stability in extrusion cooking and mentions options for the fortification of extruded products with vitamins.

## **INTRODUCTION**

Extrusion cooking is a modern high-temperature shorttime (HTST) processing technology which is gaining ground in certain industries for various reasons. Parallel to the increased applications, interest has grown in the nutritional-relevant effects of this process. Extrusion cooking in the food and feed industry is primarily applied in grain processing. Grain products are among the most important sources of B-group vitamins. Compared to more traditional thermal processing, little is known about the complex, combined effects of specific extrusion parameters on the stability of vitamins. This paper reviews the existing knowledge, and notes the possibilities to fortify extruded products with vitamins.

# CHARACTERISTICS OF EXTRUSION COOKING

This technology is able not only to manufacture innovative products, but also to produce existing ones more advantageously. Starchy raw materials, separately or in combination with non-starchy ingredients (e.g. sugar, milk powder, fat, vegetable/fruit products, salt, additives) are conveyed, mixed, and plastified in the extruder cylinder under elevated pressure and temperature. Resulting products include breakfast cereals, snacks, flat bread, textured vegetable protein (TVP), modified flours and starches, pet food, and feed for aquaculture.

Figure 1 shows the principle of an extrusion cooking plant. Extruders are generally used as the central component of an extrusion system designed for a specific appli-

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cation. They may be classified into single-screw and twinscrew systems. The extruder is fed by solids metering devices and liquid additive pumps. A drive motor transmits the required mechanical energy via a distribution gear unit to the screw shafts. Shear and kneading energy is imparted by specifically designed screws. With the controlled direct injection of steam, process variations can be achieved. On passing through the extrusion die, due to the pressure drop, a vaporisation of water leads to product expansion. The plastified and shaped material will foam and the porous structure thus formed remains. A rapidly rotating knife cuts the shaped product to length. Through the extruder, raw materials can be converted, as required, into semi-manufactured or finished products in only 30-60 s. Downstream the dryer/roaster, coating equipment, roll mill and cooling devices may follow. A wide range of processing variables can be used to influence the operation of the extruder and the characteristics of the product (Table 1; Linko et al., 1981).

#### Nutritional changes during extrusion

Extrusion cooking influences the nutritional quality of food and feed in ways both positive and negative. Reviews of chemical changes affecting nutrition during extrusion cooking have been published by Cheftel (1986), Asp & Björck (1989), Camire *et al.* (1990), and Jansen (1991). Table 2 summarises these changes.

# Effects on vitamins

Depending on their different chemical structure, vitamins have different stability properties. Degradation depends on specific parameters during food processing and storage, e.g. temperature, oxygen, light, moisture,

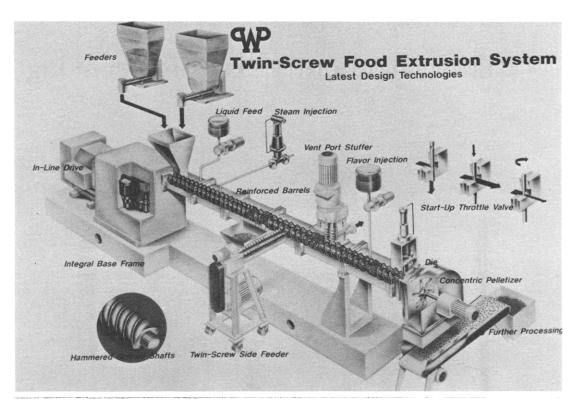


Fig. 1. Twin-screw food extrusion system. Reproduced by courtesy of Werner & Pfleiderer GmbH, Stuttgart, Germany.

pH, and obviously time. More than the usual combinations of such parameters are involved in extrusion cooking (Table 1).

The first studies on vitamin stability during extrusion were published more than 20 years ago. At that time the main function of extrusion was not real extrusion cooking, but the inactivation of heat labile growth inhibitors under relatively mild heat treatment, e.g. in soya bean products. Later investigations were usually carried out on single-screw laboratory extruders with low throughputs of a few kg/h only. Generally it was very difficult to assess the influence of a single production parameter due to the various other functional

Table 1

correlations. Sometimes several parameters were altered

simultaneously during these tests. Pham and Del Rosario (1986) and Guzman-Tello and Cheftel (1987) started to assess the effects of HTST extrusion cooking on vitamin stability using mathematical models. Thiamin has been investigated most frequently, followed by riboflavin, ascorbic acid and vitamin A. Very few studies dealt with other vitamins of the B-complex or vitamin E. No data are available for vitamin D and vitamin K. A synopsis of most relevant studies is shown in Table 3. Some of the findings

Table 2. Effects of extrusion cooking

| 1. Processing variables of extrusion cooking.                        | Effect on                              | Positive  | Negative   |  |
|--|--|---|--|--|
| Raw materials/ingredients<br>Preconditioning treatment               | Carbohydrates                          | Starch modification<br>Increased digestibility<br>Flavour development         | Maillard reaction<br>Hydrolysis                                      |  |
| Moisture content<br>Process length                                   | Proteins                               | Increased digestibility   | Destruction of amino acids   |  |
| Barrel temperatures<br>Screw configuration<br>Screw rotation speed   |  | Denaturation  | Maillard reaction; cross<br>linkages<br>Formation of<br>lysinoalanin |  |
| Fill factor of screws  | Lipids                                 | Increased digestibility<br>Fat-starch complex formation                       | Increased rancidity<br>Destruction of PUFAS                          |  |
| Discharge die design<br>Steam injection into the barrel<br>Degassing | Fibres                                 | Increased digestibility<br>Reduction of volume<br>Destruction of phytates     | Increased digestibility<br>Reduction of volume                       |  |
| Dependent on the above parameters:                                   | Vitamins<br>Minerals<br>Microorganisms | Increased bioavailability<br>Destruction                                      | Destruction  |  |
| Product temperature<br>Residence time of product<br>Throughput       | Enzymes                                | Inactivation, e.g. lipase,<br>peroxidase, lipoxigenase,<br>myrosinase, urease | Inactivation,<br>e.g. amylase, phytase                               |  |
| Pressure   | Antinutritional<br>components          | Inactivation, e.g. trypsin<br>inhibitors, lectins                             |  |  |
| Viscosity<br>Power consumption, specific energy                      | Toxic<br>components                    | Inactivation, c.g.<br>glucosinolate, gossypol,<br>glycoalkaloids, aflatoxin   |  |  |
| Functional properties of product<br>Chemical/nutritional changes     | Flavour                                | Reduction of undesirable<br>flavours  | Loss of desirable<br>flavours  |  |

| Table 3. Effects of ext | rusion cooking on vitamins |
|-------------------------|----------------------------|
|-------------------------|----------------------------|

| Parameters <sup>a</sup>                 | Vitamin                | Retention(%) | <b>Remarks</b> <sup>a</sup>  | References                    |
|---|------------------------|--------------|--|-------------------------------|
| nactivation of growth inhibitors        | Α                      | 47           |  | de Muelenaere & Buzzard (1969 |
| <b>0</b>                                | С                      | 67           |  |                               |
|   | Niacin                 | 97           |  |                               |
| n: 115–175°C                            | B <sub>1</sub>         | 90           | Encapsulation  | Smith (1969)                  |
| nactivation of                          | B <sub>2</sub>         | 91           | Not effective  |                               |
| rowth inhibitors                        | -2                     |              |  |                               |
| x: 149/193℃                             | <b>B</b> <sub>1</sub>  | 19-90        | ↑ t· B. J· B. →  | Beetner et al. (1974)         |
| /: 13/16%                               | $\mathbf{B}_{2}$       | 54-125       | $ \begin{array}{c} \uparrow \text{ t: } \mathbf{B}_1 \downarrow; \mathbf{B}_2 \rightarrow \\ \uparrow \text{ rpm: } \mathbf{B}_1 \downarrow; \mathbf{B}_2 \downarrow \end{array} $ | Deether et ul. (1974)         |
| m: 75/125                               | <b>D</b> <sub>2</sub>  | 54-125       | $\mathbf{p}_1 \mathbf{v}_1 \mathbf{v}_1 \mathbf{v}_2 \mathbf{v}_2$   |                               |
| x 177–232°C                             | D                      | 0–76         | $\uparrow$ t: <b>B</b> <sub>1</sub> ↓; <b>B</b> <sub>2</sub> →   | Bootmon at al. (1076)         |
|   | <b>B</b> <sub>1</sub>  |              | $\uparrow$ 1. $\mathbf{D}_1 \mathbf{\psi}, \mathbf{D}_2 \rightarrow \mathbf{\uparrow}$   | Beetner et al. (1976)         |
| 1/2                                     | B <sub>2</sub>         | 35–90        | 1 w: not significant   |                               |
| 1/8 resp.                               |                        |              | $\uparrow$ d: B <sub>1</sub> $\uparrow$  |                               |
| 16 in                                   | 0                      | 22.07        |  |                               |
| : 70–160°C                              | C                      | 32-86        | $\uparrow t: \mathbf{B}_{1} \downarrow_{i} C \downarrow$   | Maga & Sizer (1978)           |
| 25-59%                                  | B <sub>1</sub>         | 22–97        | $\uparrow$ w: $\mathbf{B}_1$ $\uparrow$ ;  |                               |
| 0.84-7.4                                |                        |              | •  |                               |
| m: 40–200                               | C                      | 43-97        | ↑t:C↓  | Maga & Cohen (1978)           |
| : 135–177°C                             | B <sub>1</sub>         | >85          | ↑ rpm: C↓  |                               |
| ie shape                                | •                      |              | ↑ d: C↑  |                               |
| rew configuration                       |                        |              | Sensory best product   |                               |
|   |                        |              | with lowest retention  |                               |
| /40 ppm vitamin A                       | Retinol                | 83-95        | ↑ rpm: A↑  | Lee et al. (1978)             |
| m: 700–1100                             | R. acetate             | 90–100       | ·  |                               |
| : 130°C                                 | R. palmitate           | 80-91        |  |                               |
|   | 1                      |              |  | Longer & Longer (1090)        |
| activation of growth inhibitors         | C                      | 93-110       |  | Lorenz & Jansen (1980)        |
| - 200°C                                 | Others                 | 89–110<br>28 | Describes data 1   |                               |
| : 200°C                                 | A                      | 38           | Provides data about protein  | Grebaut et al. (1983)         |
| : 36%                                   | C                      | 92<br>50     | damage and storage   |                               |
| 30                                      | $\mathbf{B}_1$         | 68           | losses (12 months)   |                               |
| m: 40                                   | B <sub>2</sub>         | 83           |  |                               |
| : 150°C                                 | Bl                     | 38–65        | $B_1$ , $B_6$ , $B_{12}$ , folate:<br>$\uparrow$ f: all $\uparrow$   | Killeit & Wiedmann (1984)     |
| m: 300                                  | B <sub>6</sub>         | 71-83        | $\uparrow$ f: all $\uparrow$   |                               |
| : 16–24%                                | B <sub>12</sub>        | 65–96        | ↑ w: all↑  |                               |
| 63-105                                  | Folate                 | 35-45        |  |                               |
|   | B <sub>2</sub>         | 85%          | $\uparrow$ specific energy: all $\downarrow$   |                               |
|   | Niacin                 | 80%          | speenie chergy. un v   |                               |
| 500                                     | B <sub>1</sub>         | 62%          |  |                               |
| 500                                     |                        |              | Final dening with ant  |                               |
|   | B <sub>6</sub>         | <b>90%</b>   | Final drying without   |                               |
|   | B <sub>12</sub>        | <b>99%</b>   | significant influence  |                               |
|   | Folate                 | 56%          |  |                               |
|   | Pantothenate           | 91%          |  |                               |
|   | Biotin                 | 74%          |  |                               |
| : 175–185°C                             | E                      | 34–76        | Free tocopherols   | Appelt (1986)                 |
| n: 115–130°C                            | B <sub>1</sub>         | 27–70        |  |                               |
| : 11-14%                                | -                      |              |  |                               |
| 50-60                                   |                        |              |  |                               |
| n: 93–132°C                             | B <sub>1</sub>         | 12-42        | ↑ t: B <sub>1</sub> ↓  | Pham & Del Rosario (1986)     |
| 30-45%                                  | 1                      |              | $\uparrow \mathbf{w}: \mathbf{B}_{1}\uparrow$  |                               |
| m: 10–30/100–200                        |                        |              | $\uparrow$ rpm: <b>B</b> <sub>1</sub> $\downarrow$   |                               |
| I value: 6·2–7·4                        |                        |              | $\uparrow pH: B_1 \downarrow$  |                               |
| ecial application                       | A.acetate              | 48 (ald)     | Includes 2 month stars as (-+)   | Putnam (1986)                 |
|   | n.autiale              | 48 (old)     | Includes 2 month storage (rt)  | Putnam (1986)                 |
| orm ROVIMIX type P                      | р                      | 84 (new)     | See above  |                               |
| $1-0.7\% B_1-HCl$                       | Bi                     | 25-95        | $\int \mathbf{t} \cdot \mathbf{B}_1 \downarrow$  | Guzman-Tello & Cheftel (1987) |
| : 30                                    |                        |              | 1 w: Β <sub>1</sub> 1  |                               |
| n: 131–168°C                            |                        |              | $\uparrow$ rpm: <b>B</b> <sub>1</sub> $\downarrow$   |                               |
| : 100–210°C                             |                        |              | -  |                               |
| 13-3-28-5                               |                        |              |  |                               |
| m: 25–150                               |                        |              |  |                               |
| i: 148−197°C                            | Е                      | 11-21        |  | Hakansson et al. (1987)       |
| : 14.6-24.6%                            | $\tilde{\mathbf{B}}_1$ | 4258         |  |                               |
| om: 200                                 | Folate                 | 78           |  |                               |
| 19                                      |                        |              |  |                               |
| 24 1-41 4                               |                        |              |  |                               |
| : 125–200°C                             | $\beta$ -carotene      | 2762         | $\uparrow$ t: carotene $\downarrow$  | Gurman Talla & Ch-G-1 (1000)  |
| 125-200 C                               | preatoiene             | 21-02        |  | Guzman-Tello & Cheftel (1990) |
|   |                        |              | No effect of type of   |                               |
| m: 150                                  |                        |              | Twin-screw extruder  |                               |
| 30                                      |                        |              | <b>Λ Λ</b>   |                               |
| :14-24%                                 |                        | c            | $\uparrow$ w: carotene $\uparrow$  |                               |
| <sub>2</sub> /O <sub>2</sub> atmosphere | Minor influence        |              |  |                               |
| 5000                                    | A, D, E,               | >90          | Expansion of feed mix  | Schai et al. (1991)           |
|   | D complex              |              | and pelleting  |                               |
| m: 108°C<br>v: 65                       | B-complex              |              | and peneting   |                               |

<sup>a</sup> Abbreviations: tm, temperature of material; tb, temperature of barrel; w, water content; rpm, rotations/min; f, throughput (kg/h); d, screw diameter; and p, pressure (bar). Example:  $\uparrow$  t:  $B_1 \downarrow$  'means with increasing temperature decreasing retention of vitamin  $B_1$ .

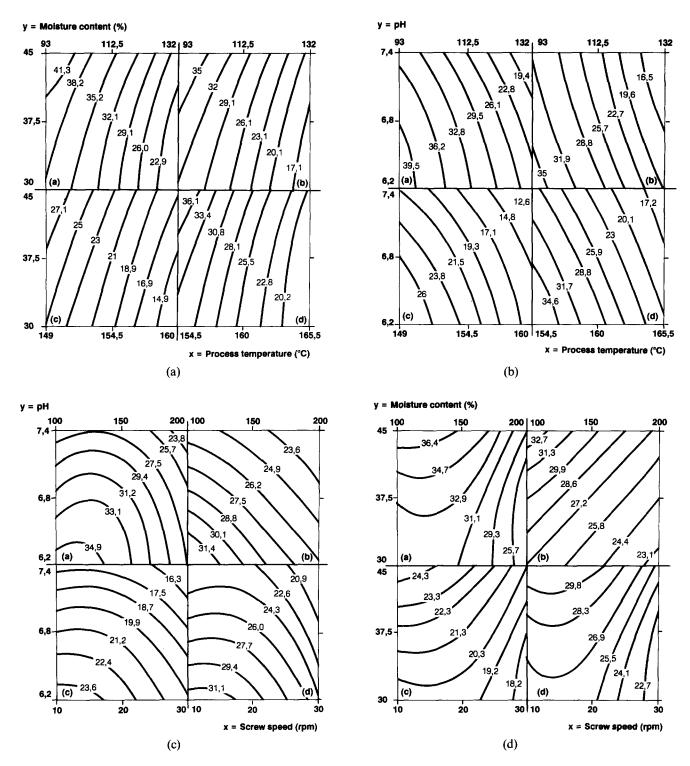


Fig. 2. Thiamine retention (in %) in extrusion cooking, dependent on process temperature, moisture content, screw speed, and pH value. (a) cowpea, (b) mungbean, (c) defatted soya bean, and (d) air classified mung bean. (Adapted from Pham & Del Rosario (1986).)

concerning the most important parameters of extrusion cooking are discussed in the following section.

As expected, the retention of vitamins generally decreases with increasing temperature and/or residence time of the material in the extruder. Only one exception has been reported. Beetner *et al.* (1974) found riboflavin stability to be improved with higher barrel temperatures.

Killeit and Wiedmann (1984) investigated the stability of B-complex vitamins during the production of extruded flat bread. The commercial crisp bread mix on the basis of 95% wheat flour T 550 contained 13% moisture. The co-rotating twin-screw extruder was operated at 150°C barrel temperature and 300 rpm screw speed. With increasing throughput the retention of vitamins  $B_1$ ,  $B_6$  and  $B_{12}$  improved. Although the extrusion pressure increases almost proportionally with the throughput or fill factor of the screws apparently the influence of the shorter residence time prevails.

An increase of initial moisture content by adding 3-11% water improved retention of the vitamins mentioned above and of folic acid. This effect can be explained by the fact that higher moisture leads to lower

viscosity of the material. As a consequence the product is less sheared and the dissipative energy input drops.

For the first time a negative correlation between the stability of thiamin, folic acid and cobalamin, and the specific mechanical energy input (kWh/kg) could be confirmed in this study. Under industrial production conditions with a throughput of 500 kg/h, the retention of thiamin, folic acid and biotin was 62, 56, and 74%, respectively. Pyridoxine, cobalamin and pantothenate suffered no significant losses. The further drying/toasting of the extruded flat bread had no significant impact on vitamin stability.

By increasing the diameter or the gap of the die, better retention could be obtained (Beetner *et al.*, 1976; Maga & Cohen, 1978).

Thiamin retention in cowpea (CP), mung bean (MB), defatted soya bean (DSB), and air classified mung bean (ACMB), texturised by extrusion, were studied by a least squares regression equation using process temperature, screw speed, buffer pH, and moisture content as the major independent variables. The increase in moisture increased retention values, while increases in the other variables decreased them. Figure 2 show thiamin retention contour maps. The average retention values were 32.5% in CP, 27.3% in MB, 21.2% in DSB, and 27.2% in ACMB (Pham & Del Rosario, 1986).

In the study of Guzman-Tello and Cheftel (1987) wheat flour with 0.1-0.7% thiamin hydrochloride was extruded. The destruction rate was almost independent of the initial thiamin concentration. Retention of thiamin decreased from 88.5 to 57.5% when the product temperature increased from 131 to 176°C. Other parameters were kept constant at 13.7% moisture, 100 rpm screw speed, 30 kg/h feed rate and approx. 41 s residence time in the heating zone. More thiamin was retained by increasing the moisture content, while again higher screw speed caused higher losses. The results indicate that thiamin destruction follows an apparent first-order reaction. The rate constant k of destruction, calculated from near isothermal extrusion experiments at 133, 142 or 152°C, follows an Arrhenius relationship with an activation energy of 49.9 kJ/mol. By means of a mathematical model, prediction of the extent of thiamin destruction seems possible. However, the equation applies only to the experimental range studied here.

The suitability of thiamin as an indicator substance of thermal processes is well known, based on many kinetic studies. Another of the exceedingly rare kinetic investigations about extrusion stability dealt with the provitamin A:  $\beta$ -carotene (Guzman-Tello & Cheftel, 1990). This substance is not only an important and safe source of vitamin A but also a useful food colour. There is considerable evidence that  $\beta$ -carotene, being a highly active singlet oxygen quencher, may play an important role in the prophylaxis of free radical mediated diseases. The thermal and/or oxidative colour loss from a wheat flour/all-*trans*  $\beta$ -carotene (80 ppm) mix followed first order kinetics. The overall rate constant k of colour loss reflects the intensity of extrusion processing.

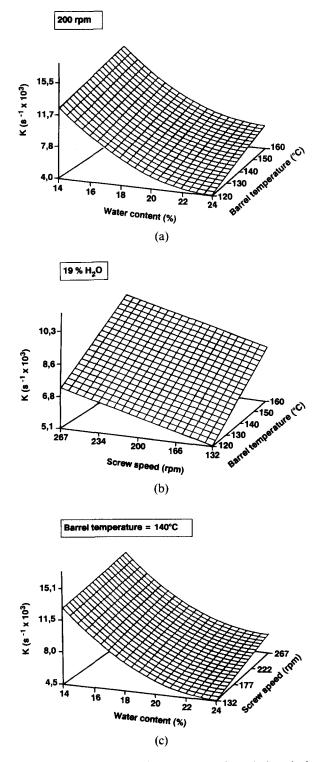


Fig. 3. Colour loss due to beta-carotene degradation during extrusion cooking. (Adapted from Guzman-Tello & Cheftel (1990).)

Consistent with the findings mentioned above, k-values of degradation increased with decreasing water content of the mix and with increasing barrel temperature (Fig. 3). The results were independent of the type of twinscrew extruder. Extrusion under N<sub>2</sub> or O<sub>2</sub> or in presence of an antioxidant slightly affected colour loss, confirming that degradation is mainly due to thermal inactivation. Within a barrel temperature range of 125-200°C, 38-73% of the initial all-*trans*  $\beta$ -carotene was destroyed. Free tocopherols show antioxidative effects in vitro and in vivo. Hakansson et al. (1987) investigated the effects of various thermal processes on protein quality, vitamins and selenium content in wheat products. They found that natural tocopherols were far more labile during extrusion cooking than thiamin. Retention was 11-21% and 42-58%, respectively. With a retention of around 80\%, folic acid proved to be quite stable.

# VITAMINS — COMPOUNDS AND FORMS OF APPLICATION

Naturally occurring substances with vitamin activity, e.g. pyridoxine compounds, can have very different stability properties (Labuza & Kamman, 1982). For certain vitamins, more than one compound with vitamin activity is available and permitted for nutritional enrichment. In the case of vitamin  $B_1$ , thiamin hydrochloride or thiamine mononitrate are potential sources with different stability (Gregory & Kirk, 1978). Another example is provided by tocopherol. Free tocopherols are extremely sensitive to oxygen which is why they are used as antioxidants for fats and oils. On the other hand, the esterified form, tocopherol acetate, is very stable and just right for enrichment

It is possible to improve the stability properties of vitamins by modification of the molecule or of the form of application. The first option can be realised in very specific cases only. Vitamin C for extruded fish feed serves as an example. Ascorbic acid normally shows poor stability during extrusion. Coelho (1991) reported ascorbic acid as the most sensitive of the vitamins. However, L-ascorbyl-2-polyphosphate (AsPP) represents a very stable and commercially available form of vitamin C for feed applications. Digestive enzymes present in the intestine of the animal break down the compound into ascorbic acid and residual phosphates. Complete bioavailability was demonstrated by Grant et al., (1989). The average retention of traditionally coated ascorbic acid (with ethylcellulose) and AsPP during extrusion of catfish feed were 39% and 83%, respectively. The important factor is to keep the biological activity after extrusion as high as possible during the subsequent storage. After 28 days storage at 25°C, 78% of the residual ascorbic acid in the coated form was lost while no degradation was reported for AsPP (Robinson et al., 1989).

What about the second option? Vitamin A, e.g. as retinol acetate, is a readily oxidised vitamin. Water dispersible application forms are produced by spray drying or powder catch processes. The matrix of the powders normally consists of gelatine and sucrose. By gelatine crosslinking, a more durable and resistant coating is achieved. Contact between vitamin A in the matrix and water or aggressive ingredients such as trace minerals is then minimised. Such protected bead forms are superior to conventional coated products in extrusion cooking (Putnam, 1986).

## ADDITION/COEXTRUSION/POST-EXTRUSION

Taking the above-mentioned destructive factors into account, post-extrusion application of vitamins seems to show up to advantage in comparison with coextrusion application (Schlude, 1987). Suitable plants for enrobing and coating of extruded products are described and available (Treier, 1991). These allow the addition of dry ingredients like salt or spices, and the spraying with colours, flavoured oils, sugar solutions, or even with chocolate. At the same time, vitamins can be applied.

## SUMMARY

Extrusion cooking (HTST) represents a very efficient processing technology, which enables the manufacture of a wide variety of food and feed products on the basis of grain produce. What distinguishes this technology is the variety of process parameters and their impact on product quality.

The effects of extrusion cooking on nutritional quality are ambiguous. Positive effects can be seen in increasing digestibility or inactivation of undesirable substances. However, as far as vitamins are concerned, the main effects reported are destructive.

Generally, the retention of vitamins in extrusion cooking decreases with

- increasing temperature
- increasing screw speed
- decreasing moisture
- decreasing throughput
- decreasing die diameter
- increasing specific energy input

In practice, these parameters are unlikely to be optimised to ensure minimal vitamin losses, because a compromise on production and product concepts is difficult. Depending on the vitamin concerned, considerable degradation can occur, especially in products with high sensory appeal. The following options for the nutritional enrichment of extruded products with vitamins are possible.

- Application of more than the necessary amount to compensate for losses during coextrusion and storage.
- (2) Post-extrusion application, e.g. by dusting, enrobing, spraying, coating, or filling, together with other ingredients.
- (3) Usage of specific vitamin compounds or forms of application with improved stability.

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