Application of supercritical carbon dioxide extrusion in food processing technology

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Abstract
Extrusion process is one of the most important innovations of the 20th century applied in many industries. Extrusion is a technology that is increasingly used for the production of various food products, especially snacks and breakfast cereals. Supercritical carbon dioxide (CO_2) as a non-toxic, non-flammable and inexpensive, is applied in many processes, including the extrusion technology. Supercritical CO_2 extrusion process (SCFX) found its application primarily in the processing and manufacturing plastic, but recently more and more begins to be applied in food production and processing. Scientific researches in this area are based in production of extrudates with improved properties compared to conventional extrusion process without the addition of CO_2. A number of applications of SCFX in food processing technology will be reviewed and numerous advantages over the conventional process will be described in this paper.

Keywords: extrusion, supercritical CO_2, food technology.

Available online at the Journal website: http://www.ache.org.rs/HI/

REVIEW PAPER

UDC 663/664:546.264–31:66.02

Hem. Ind. **71** (2) 127–134 (2017)

Health and nutrition are the most challenging fields today and this trend will continue in future as well. Decrease of nutritional quality of foods, because of the high temperature during processing is challenge in most traditional cooking methods that can be met with a few different processing techniques. One such method is extrusion cooking, which is better than the other food processing techniques because it is continuous process, versatile, low cost, environmentally--friendly with high productivity, product quality and significant nutrient retention, causing by the high temperature and short time required (high operating temperatures (up to 200 °C) and pressures (over 10 MPa) as well as high shear rates) [1–3].

Extrusion process is one of the most important innovations of the 20th century, and it is presented as a model of scientific and technology transfer between different processing industries, such as the polymer and plastics, food and feed, and paper-milling industries in particular. It is a process of converting a raw material into a product of uniform shape and density by forcing it through a die under controlled conditions. Functions of extruder which can be used for a wide range of food, feed and industrial applications are: agglomeration, degassing, dehydration, expansion, gelatinization, grinding, homogenization, mixing, pasteurization and sterilization, protein denaturation, shaping, shearing, texture alteration, thermal cooking, unitizing, etc. [1,4–6].

The most popular extrusion-cooked products include: direct extruded snacks, RTE (ready-to-eat) breakfast cereal, snack pellets, baby food, instant concentrates, pet food, aquafeed, texturized vegetable protein, crispbread, bread crumbs, emulsions and pastes, baro-thermally processed products for the pharmaceutical, chemical, paper and brewing industry, different kinds of sweets, chewing gum, rice bran stabilization, precooked or thermally modified starches, flours and grain [3,7,8]. Enrichment of extruded snacks with nutritionally valuable ingredients is increasingly practised by many studies. Addition of protein and fibre rich ingredients like legumes or whey protein, or various types of flours and the addition of fruits and vegetables is widely used in the food industry, both for final products and for the modification of flours for bakery industry [9–13]. Since extrusion is a high-temperature/short time (HT/ST) process, it minimizes degradation of food nutrients and improves the digestibility of proteins (by denaturing) and starches (by gelatinizing). Extrusion cooking at high temperatures also destroys, trypsin inhibitor, and undesirable enzymes, such as lipases, lipoxidases, and micro-organisms. Other advantages of extrusion are increased digestibility of fibers, increased bioavailability of minerals, inactivation of some components *e.g.*, glucosinolate, gossypol, glycoalkaloids and aflatoxin. However, like every other process, there are some disadvantages. Carbohydrates and proteins are subjected to Maillard reactions and there

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Paper received: 29 June, 2015
Paper accepted: 17 May, 2016
https://doi.org/10.2298/HEMIND150629024P

is a risk of acrylamides and hydroxymethylfurfural formation [1].

Extrusion process can be combined with supercritical fluid, where the most commonly used fluid is environmentally friendly CO_2. The supercritical fluid extrusion (SCFX) process has a potential for producing a wide range of puffed products, with improved texture, color and taste. The use of low-temperature and low-shear process conditions offers minimum process losses of heat-labile nutrients [8, 14].

SUPERCRITICAL FLUID (SCF)

A pure component is considered to be in a supercritical state if its temperature and its pressure are higher than the critical values of pressure and temperature (Figure 1). The characteristic orders of magnitude for physical properties of gasses, liquids and supercritical fluids are listed in Table 1. In the supercritical state, liquid-like densities are approached, while viscosity is near that of normal gases, and diffusivity is about two orders of magnitude higher than in typical liquids. The density of a supercritical fluid is extremely sensitive to minor changes in temperature and pressure near the critical point. According to that, supercritical fluids have the properties between those of gases and liquids [15–18].

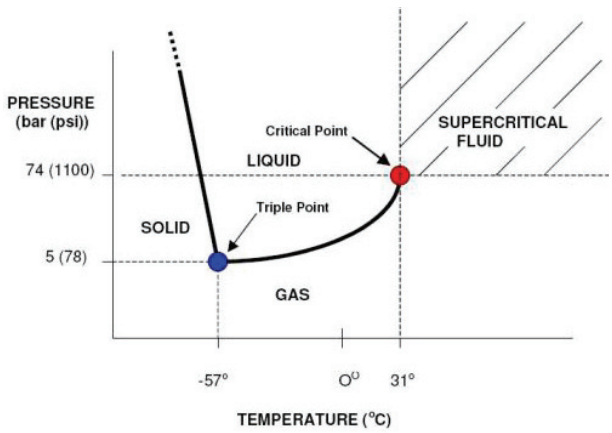

Figure 1. Phase diagram for CO_2.

Number of compounds have been examined as supercritical extraction solvents: ethane, propane, hexane, pentane, ethylene, dimethyl ether butane, nitrous-oxide, etc. In fact, any solvent can be used as a supercritical solvent; however, the technical viability (critical properties), toxicity, cost and solvation power determine the best-suited solvent for particular application [2,15,19–23].

As already mentioned CO_2 is of particular interest as SCF because of its suitable critical constants (Tc = 31.1 °C, Pc = 7.38 MPa). At the same time it is non-toxic, non-explosive and readily available [21]. Furthermore, the fact that CO_2 is a gas under ambient conditions which can be removed from the product very easy, avoiding the costly processes of drying or solvent removal, which is very important in the processing of food [24].

SCF have already been applied in several processes, in pharmaceutical, food and textile industries [25–29]. SCF have been utilized in different novel methods of food processing such as extrusion.

Supercritical fluid extrusion

Supercritical fluid extrusion (SCFX) has been developed and patented by Rizvi & Mulvaney (1992) [30]. It is process where supercritical CO_2 is injected blowing agent for control puffing in extrusion and viscosity lowering plasticizer. Extrudates have porous interior with smooth external surface. CO_2 injection serves as inexpensive alternative for expanding products at lower temperatures [31]. Supercritical CO_2 can achieve rapid solubilization by enhancing the solubility of the fluid in processing matrix and reducing surface tension effects. Solubility of CO_2 can be increased with increasing pressure or with decreasing temperature. The use of SCF in the extrusion process is based on a four--step process [8] which includes:

1) development of a dough with gas-holding properties by mixing alone or by cooking (gelatinization), mixing and cooling, if necessary, to below l00 °C, as in starch melts;

2) injection of supercritical CO_2 into the dough or melt at a rate not exceeding the saturation limit, and mixing to create a single phase within the extruder barrel;

3) creation of a controlled thermodynamic instability by manipulation of the pressure and/ or temperature in the extruder;

4) control of the degree of cell growth during the setting of the product through appropriate die selection and post-extrusion drying and cooling processes.

SCFX operating parameters such as the injection rate of supercritical CO_2 and rate of pressure drop are critical and can be adjusted to produce broad range of cell size, density and product expansion. Pressure profile across the extruder barrel can be attributed to the

Table 1. Characteristic orders of magnitude of gas, liquid and supercritical state

State of solvent	Density, $g cm^{-3}$	Diffusivity, $cm^2 s^{-1}$	Viscosity, $g cm \cdot s^{-1}$
Gas	10^{-3}	0.1	10^{-4}
Liquid	1	5×10^{-6}	10^{-2}

implemented screw configuration and die dimension. Liquid CO_2 is first cooled and then compressed to above its supercritical pressure. Then, the high pressure CO_2 is heated well into its supercritical phase. This CO_2 can be directly injected into the extrusion process under pressure into a fully cooked dough in the extruder. Expansion or puffing of the product occurs by gas expansion and diffusion, the expansion occurring gradually from inside to outside, leaving a central core of empty space and a naturally formed expanded outer layer or skin. Shematic diagram of supercritical CO_2 system together with extruder system is shown at Figure 2.

Temperature control of supercritical CO_2 is very important to maintain a stable density troughout the system. After introduction into the process, it is uniformly distributed throughout the product and with precisely controlling the flow of supercritical CO_2 very stable and easily adjusted expansion for the end product can be obtained [32]. Supercritical CO_2 changes the rheological properties of the material inside the extruder and it produces products with less intensive puffing, resulting in a smoother surface and more uniform internal cell structure [14]. Supercritical CO_2 is an effective plasticizer for starch – water mixture, lowering the viscosity of the melt. It can also be used to adjust the pH of the product in extruder (through in barrel formation of carbonic acid). In some applications, usage of lower temperatures (less than 100 °C) and the presence of supercritical CO_2 can allow avoiding the use of water as expansion agent. Results are seen in the reduction of the product humidity and the formation of steam during pressure drop [2]. SCFX process brings visual, functional and textural novelty to the existing food products. Products have smooth outer surface and they are uniform regulary-shaped with unconnected internal pores. Specific mechanical energy (SME) input of extrusion process without CO_2 gas injection is significantly higher than those of extrusion process with CO_2 gas injection. Low temperature extrusion and significantly reduced pressure at the exit die prevent damage of heat sensitive components and labile nutrients thus permitting the production of new functional food products or ingredients and flavor and bioactives encapsulation on the interior surface of cellular structure [30,32].

Some of the most important advantages of SCFX are:

- production of extruded products on low temperatures and low-shear expansion;
- dual texture (porous interior with smooth external surface), with variable number and size of cells for texture control;
- manipulation of in-barrel pressure and temperature during processing offers added opportunities for generation of microcellular, composite (sandwich) structures of different morphologies and mechanical properties;
- possibility of adding heat sensitive ingredients (flavorings, colorants, etc.);
- option of reactive extrusion via pH control through in barrel formation of carbonic acid;
- reduction of melt viscosity and pH (due to large solubility effects) provide more degrees of freedom to modify the rheological and chemical properties of the extrudates [1,2,8,14,21,26,30,32].

According to all of these advantages it is possible to produce large list of products with SCFX, such as: breakfast cereals, snack foods, pasta, chocolate and confectionery, coffee, leavened of dough and bread, milk protein and whey protein crisps, etc., with improved properties and better nutritional quality, than using conventional extrusion.

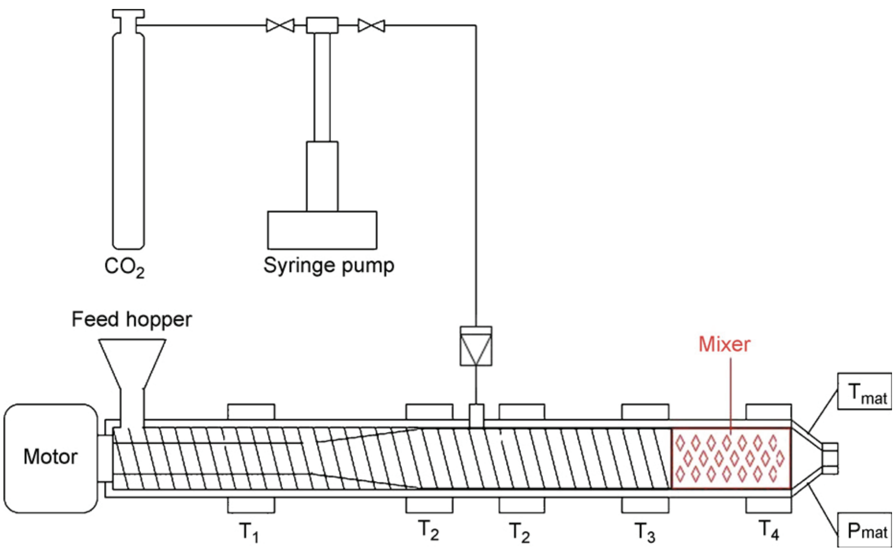

Figure 2. Shematic diagram of SCFX extruder [5].

APPLICATION OF SCFX IN FOOD TECHNOLOGY

The usage of supercritical CO_2 in the extrusion process is widely applied by many scientists. At first, it was only applied to the processing of different polymers, but today is increasingly used in food processing technology. Primarily, the possibility of applying extrusion with supercritical CO_2 for the production of extrudates at lower temperatures is examined, that reduces energy costs, but also ensures a better quality product and preservation of thermally labile substances in food [31,33–38]. Scientific research in the field of SCFX and application of supercritical CO_2 in food technology has significantly increased in the last three decades and in this paper the published works in this field are summarized. Comparison of classical extrusion and extrusion with the addition of CO_2 on thiamine and riboflavin content in corn extrudates were examined by Boyaci *et al*. (2012). They concluded that the process of cold extrusion with the addition of CO_2 can modify the structure of corn extrudate, and increase retention of valuable thermo-labile substances such as thiamine [31].

Paraman *et al*. (2012) used SCFX to produce shelf-stable puffed rice fortified with protein, dietary fiber, and micronutrients. Supercritical CO_2 served as a viscosity-lowering plasticizer and blowing agent during the process. The SCFX process allowed for the complete retention of all added minerals, 55−58% retention of vitamin A, and 64−76% retention of vitamin C. All essential amino acids including lysine were retained at exceptionally high levels (98.6%), and no losses were observed due to Maillard reaction or oxidation. Authors in this study have demonstrated that the SCFX process can be used in the production of cereal-based products fortified with multiple macro- and micronutrients and therefore can be effectively used to address multi-nutrient deficiencies in targeted populations [39].

Jeong and Toledo (2004) examined the possibility of applying supercritical CO_2 in the production of extrudates with pre-gelatinized rice flour in the twin-screw extruder at low temperatures (40–60 °C) in order to improve the expansion. They concluded that CO_2 extrusion gives very porous products, easily soluble in water [38].

Cho and Rizvi (2009) investigated influence of melt rheology and processing conditions on the expansion and 3D microstructure of biopolymeric foams produced by SCFX. Results showed that flow behavior index increased with the addition of supercritical CO_2, the lowest n value was observed for all formulations with no supercritical CO_2 addition. This suggests that supercritical CO_2 acted as a plasticizer by reducing amylose entanglement density. Although supercritical CO_2 had the melt viscosity reduction effect, SCFX expansion increased when supercritical CO_2 was injected up to a 0.5 wt.% ratio to feed [40].

Patel *et al*. (2009) have developed cross-linked starch microcellular foam by solvent exchange and reactive supercritical fluid extrusion. Some results showed that presence of CO_2 during extrusion of starch crosslinked with epichlorohydrin (EPI) caused an increase in the pore number concentration of the materials and also the appearance of a bimodal pore size distribution. Larger pores were found to be mostly in the center of the extrudate whereas smaller pores tended to be toward the exterior of the extrudate. The crosslinked and CO_2 extruded samples were the only extruded samples that showed a significant increase in the water swelling for solvent exchanged extruded samples relative to the corresponding air dried sample [41].

Using supercritical CO_2, Alavi and Rizvi (2005) tried to enhance expansion in starch-based microcellular foams. They also tried to solve problem of high effective diffusivity of CO_2 in the porous matrix which favors escape of the gas to the environment, reducing the amount available for diffusion into the bubbles. They had two approaches to solve the problem: increasing the nucleation rate and the final bubble density in the foam and reducing the melt temperature. They concluded that both strategies are useful in controlling and enhancing expansion, confirming it with determination of textural properties of the expanded food product [42].

Chen and Rizvi (2006) examined rheology and expansion of starch water–CO_2 mixtures with controlled gelatinization by supercritical fluid extrusion. Supercritical CO_2 was shown to be an effective plasticizer for starch water mixture at 0.45 g SC-CO_2/100 g sample, reducing the viscosity of the melt by an average of 14%. Supercritical CO_2 was a good blowing agent producing nonporous skin and distinct expanded microcellular morphology for the starch-water mixtures with degree of starch gelatinization at or above 80% [43].

Phosphorylated cross-linked starch produced by extrusion with supercritical CO_2 may be desirable for use as biodegradable material because of its good resistance to water [36].

Ayoub and Rizvi (2008) investigated the properties supercritical fluid extrusion-based crosslinked starch extrudates. Starch microcellular foam was produced by SCFX using native and pregelatinized starch mixtures. SCFX process showed a high degree of control over the extrudate expansion and microstructure can be achieved by varying the rate of injection of supercritical CO_2. The results obtained showed that reactive extrusion of starch with epichlorohydrin with supercritical carbon dioxide as a blowing agent offers a promising new technique to generate microporous foams for use in various applications [44].

Alavi *et al.* (1999) examined structural properties of protein-stabilized starch-based supercritical fluid extrudates. They used SCFX to produce pre-gelatinized corn and potato starch-based extrudates with addition of 4–10% thermosetting egg white or whey protein concentrate. Expansion ratio of extrudates increased up to 341% and bulk density decreased up to 74% as the extrusion temperature was raised from 22 to 100 °C. The best expansion, while maintaining an intact cellular structure, was observed for samples extruded at 85 °C containing 7% white egg or 7% whey protein concentrate [45].

The application of SCFX in the production of texturised whey protein concentrate was tested by Manoi and Rizvi (2008). They found that SCFX gives the texturised whey protein concentrate effective for improving the texture of food in a wide temperature range [37].

Furthermore, Nor Afizah *et al*. (2012) and Nor Afizah and Rizvi (2014) worked on texturization of whey protein concentrate via SCFX and produced a new whey protein concentrate ingredient that is able to form cold-set protein gels and emulsion gels at room temperature. They concluded that texturized whey protein concentrate generated by low and high temperature extrusions can thus be utilized for different products requiring targeted physicochemical functionalities. Texturized whey protein concentrate extruded at 50 and 70 °C formed soft-textured aggregates with higher solubility than products extruded at 90 °C which formed protein aggregates with lower solubility. Reactive supercritical fluid extrusion (RSCFX) process of whey protein concentrate at 50 and 70 °C caused only a minimal loss of protein solubility, whereas at 90 °C proteins were extensively denatured, causing a considerable increase in aggregates size and a reduction in solubility [46,47].

Cho and Rizvi (2008) investigated time-delayed expansion behaviour of SCFX extrudates via video analysis. The results showed that the initial cross-sectional expansion of SCFX extrudate depends on time, supercritical CO_2 concentration and pressure drop rate. Compared to typical growth time of steam-based extrudates, growth time of SCFX extrudates was approximately 30–200-fold longer. It was observed that a high pressure drop rate is suitable for getting a larger expansion ratio for the starch-based SCFX formulation. Using 5.9 mm die showed significant structure collapse because of gas loss. However, size volume ratio of SCFX extrudates can be controlled using small die [48].

Ondo *et al*. (2013) examined the effect of temperature extrusion, alkalized cocoa powder and the addition of CO_2 in production of extruded cornmeal. They found that the addition of CO_2 can get the product with unique porous structure and good texture properties [34].

Sokhey *et al.* (1996) used SCFX in cereal processing, to make low-density breakfast cereals with increased bowl life and improved texture. Supercritical CO_2 was injected into the cereal melt in a high-pressure zone within the extruder, which was developed and maintained by a combination of screw configuration, feed rate and in-barrel moisture content. The SCFX extrudate had 23% water absorption as opposed to 36% for steam puffed extrudate when placed in a 100% rh environment. SCFX extrudate showed less darkening after extrusion and drying at high temperature as compared to an extrudate without CO_2, when diary ingredients were added [49].

Application of SCFX technology is possible also in the production of leavened dough without yeast through supercritical CO_2 injection into the batter. This substantially reduces the time of manufacture of dough, and thus the total costs of production [35].

Effect of germination and the SCFX on the physicochemical properties of wheat extrudate was examined by Singkhornart *et al*. (2014). Based on the results of research they concluded that extrusion temperature, screw speed and CO_2 addition have significant effect on physical properties in relation to nutritional value. Addition of CO_2 not only improved expansion at lower temperatures, but also showed a significant effect on the color and the content of reducing sugars, which are associated with the Maillard reactions and caramelization [33].

An interesting research on the properties of corn grits extrudates enriched with corn fiber produced by extrusion with and without CO_2 addition was conducted by Wang and Ryu (2013). They concluded that the extrusion temperature is an important factor on physical properties of the extrudates in both types of extrusion. Addition of supercritical CO_2 gives better results at a lower temperature extrusion (90 and 105 °C), as compared to higher temperature (120 °C). With addition of CO_2 surface of the extrudate is smoother and their fragility is less. The extrudates obtained at lower temperatures with the addition of CO_2 had better distributed air spaces, with thin walls. Color and antioxidant properties of the extrudate are relatively stable in the extrusion at a higher temperature (120 °C) with the addition of CO_2, compared to the extrusion without the addition of CO_2. Water absorption index increased after the extrusion process with most pronounced effect at the extrusion with the addition of CO_2 [50,51].

Effects of processing parameters on physical properties of corn starch extrudates expanded using supercritical CO_2 injection was investigated by Lee *et al*. (1999). The expansion ratio measured with supercritical CO_2 extrudates was relatively low, and as a result, bulk density (>0.3 g/cm^3) was greater than for normal extrudates (0.1–0.2 g/cm^3). On water solubility and absorption SCFX had positive effects, water solubility was relatively low (<3%) for all supercritical CO_2 treatments compared with values from normal steam-expanded extrudates. SEM photography showed that the surface of supercritical CO_2 extrudates was unusually smooth compared that of steam-puffed extrudates. Cross-sections of extrudates had uniformly distributed and closed air cells with thin cell walls [52].

Moreover, SCFX showed benefits in production of rice-soy crisps fortified with micronutrients and soy protein. The increasing soy protein fortification from 25 to 40 g/100 g reduced the crisps expansion ratio, crispiness and increased piece density, bulk density and hardness. The nutrient fortification improved protein and dietary fiber content. The extrusion process retained all of the added minerals and about 50% retention of vitamin A and C in the final products [14].

Masatcioglu *et al*. (2014) added hull-less barley flour in corn extrudates produced by conventional extrusion and CO_2 injection process. Extrudates produced with CO_2 injection process had more uniform expansion and smoother surface. There was no reducing effect on β-glucan levels with CO_2 injection, and this can be used as an alternative method for producing β-glucan supplemented breakfast cereals and snack foods [53].

Within this review we showed previous use of the SCFX in food technology and possibility of its application in production of different types of products.

CONCLUSION

The application of supercritical CO_2 extrusion enables the production of a wide range extruded quality products at lower temperatures compared to classic extrusion. It allows energy savings, affects the preservation of nutritional high-quality food ingredients, which are usually heat-labile and avoiding the formation of undesirable products during food processing at high temperatures. Supercritical CO_2 extrusion process has a lot of space for expansion and further usage both in food and in other industries.

Acknowledgments

This work has been fully supported by Croatian Science Foundation under the project 1321.

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IZVOD

UPOTREBA EKSTRUZIJE SA SUPERKRITIČNIM UGLJIKOVIM DIOKSIDOM U PREHRAMBENOJ TEHNOLOGIJI

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Ekstruzija je jedna od najvažnijih inovacija 20. stoljeća, koja se primjenjuje u mnogim industrijama. To je tehnologija koja se sve više koristi u proizvodnji različitih prehrambenih proizvoda, kao što su grickalice, žitarice za doručak, hrana za djecu, instant proizvodi, tjestenina, hrana za životinje itd. Osim za proizvodnju gotovih proizvoda, može se koristiti i za modifikaciju brašna koja se kasnije upotrebljavaju u pekarskoj industriji. Superkritični ugljikov dioksid (CO_2) se primjenjuje u mnogim procesima, uključujući i proces ekstruzije jer je netoksičan, nezapaljiv, inertan, lako se uklanja i jeftin. Ekstruzija sa superkritičnim CO_2 (SCFX) prvenstveno se upotrebljavala u proizvodnji i preradi plastike, ali u zadnje vrijeme sve se više koristi u proizvodnji i procesiranju hrane. Znanstvena istraživanja iz ovog područja temelje se na proizvodnji ekstrudata poboljšanih svojstava s obzirom na klasičnu ekstruziju. Proizvodi imaju poboljšanu, teksturu, boju i okus. Koriste se razni dodatci kako bi se dobili obogaćeni proizvodi s većom nutritivnom vrijednošću. SCFX ima pozitivno djelovanje na očuvanje nutritivnih komponenata u hrani, a kao jedna od glavnih prednosti ističe se smanjen nastanak produkata neenzimskog posmeđivanja. U ovom radu bit će prikazana upotreba SCFX u proizvodnji različitih vrsta prehrambenih proizvoda i prednost takvih proizvoda u usporedbi sa ekstruzijom bez dodatka superkritičnog CO_2.

Ključne reči: Ekstruzija • Superkritični CO_2 • Prehrambena tehnologija