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SUPERCRITICAL CO₂ EXTRUSION – NOVEL TECHNOLOGY IN FOOD INDUSTRY

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Abstract

Nowadays extrusion is an important process in food industry due to the HTST (High Temperature Short Time) effect that is applied in many processes. It is used to produce a wide variety of products, from modified starch and flours, over pasta and meat products, to snack and confectionary products.

Although it is considered to be an HTST process, it still may result in the formation of acrylamide and other compounds potentially harmful for human health. To overcome this issue, extrusion assisted with supercritical CO_2 has been introduced, opening the possibility to obtain products of retained quality at lower temperatures.

The aim of this paper is to give a short overview of research on extrusion with supercritical CO_2 and address some issues related to it.

1. INTRODUCTION

Compared to other processes, extrusion has been introduced to food industry relatively late. Nevertheless, nowadays it is a very significant and common process applied in the production of snack products, pasta, chewing gums, bonbons, breakfast cereals, modified flours, texturised proteins, etc.

When applied in food industry, extrusion often includes both high pressures and high temperatures. Since high temperatures cause unwanted reactions which result in the formation of compounds that cause adverse health effects (such as acrylamide), contemporary scientific and professional research is oriented towards the production of products without, or with reduced amounts of harmful compounds, but of the same quality. In this manner, CO_2 in supercritical state has been applied in the extrusion process.

2. EXTRUSION WITH SUPERCRITICAL CO₂

The pioneers in this research area, Rizvi and Mulvaney, patented the supercritical CO_2 extrusion process in 1992, claiming it controlled expansion and acted as a plasticiser and a viscosity modifier. In subsequent research (Rizvi, Mulvaney and Sokhey, 1995) they listed its advantages: The formation of composite microstructures at the microcellular level that result in specific morphological and mechanical properties, the potential for application of thermo-

labile additives (colours, aroma compounds, vitamins...), and viscosity reduction. Other authors (Bilgi Boyaci et al., 2012; Sharif et al., 2014) also recognised these positive aspects. In addition, lower temperature applications require lower energy costs (Bilgi Boyaci et al., 2012).



Figure 1. Scheme of an extruder with the addition of supercritical CO, at the Faculty of Food Technology Osijek

All these advantages resulted in very extensive research on supercritical CO_2 extrusion in the field of biopolymers and plastics production. Chauvet et al. (2017) made an extensive overview of current research on biopolymer production using this process.

To ensure that a process with supercritical CO₂ is successful, incorporation of CO₂ into the gelatinised mass has to be addressed during the design phase of the extrusion process, because CO₂ "backflow" can occur due to the high pressure within the barrel. It can be prevented by the placement of a ring on the zone transition, or "tandem" extrusion can be applied, where the compression of the material and the incorporation of supercritical CO₂ are performed in the first extruder, and additional homogenisation and partial cooling are performed in the second extruder (Chauvet et al., 2017).

Generally, it is considered that supercritical CO_2 results in a uniform porous structure, but slower expansion than in the classical process has to be taken care of. In addition, the large pressure drop at the exit from the extruder can result in structure collapse and loss of expansion due to gas leakage from the product (Cho and Rizvi, 2008). This problem can be resolved by partial cooling in the twin screw extruders before the introduction of the material to the die or by reducing the die diameter (Alavi and Rizvi, 2005). Although it is still not extensively researched in food technology, some examples of successful applications of supercritical CO_2 extrusion in food production have been reported in scientific literature. Paraman et el. (2012) reported that supercritical CO_2 application in the production of puffed rice results in the preservation of all essential amino acids and over 50% of vitamins A and C. The results of this research have been confirmed on rice crisps with the addition of soy protein and micronutrients (Sharif et al., 2014), and satisfactory results have been reported for rice crisps with spirulina, minerals, and vitamins A and C (Bashir et al., 2016).

Masatcioglu et al. (2014) applied supercritical CO₂ extrusion in the production of corn extrudates with the addition of hull-less barley flour. Compared to the classical process, extrudates produced with supercritical CO₂ had smoother texture and more uniform expansion, and all other properties were comparable to the classical product. In wheat extrudates, supercritical CO₂ extrusion enhanced the expansion and lightness of the products, without significant influence on the chemical composition (Singkhornart et al., 2014).

Modified flours produced using this process are readily soluble in water (Jeong and Toledo, 2004), and supercritical CO_2 extrusion can replace yeast fermentation and ensure continuity of dough expansion in bread production (Hicsasmaz et al., 2003).

Manoi and Rizvi (2008, 2009) applied supercritical CO_2 extrusion in the production of texturised whey protein. They reported that gel formation in cold water enables the application of this product in modification and texture formation of food, especially when texturisation was performed at low pH, when smooth structure and creamy texture were obtained.

Ruttarattanamongkol et al. (2015) reported that texturised whey proteins produced by supercritical CO_2 extrusion can be used in the stabilisation of oil emulsions with different oil content and consistency – from salad dressings to spreads, and Cho and Rizvi (2008) successfully applied it in corn chips. They reported that supercritical CO_2 enabled extrusion at temperatures below protein denaturation, which in turn prevented hard texture formation.

Paraman et al. (2013) produced fructo-oligosaccharide-enriched whey protein crisps by using supercritical CO_2 extrusion. The sensorial acceptable product contained 8% of prebiotic fibre and 80% whey, and had even porous structure and crispness, with 92% preserved essential amino acids.

Supercritical CO_2 extrusion was a good tool for pore size and water-solubility control in starch modification, and phosphorylated starch produced in this process can be used in the production of biodegradable packaging due to low mass, high water resistance, and characteristic non-porous foamy structure (Patel et al., 2009; Manoi and Rizvi, 2010).

At the Faculty of Food Technology Osijek, as part of the project "Application of Food Industry By-products in the Development of Functional and Environmentally Friendly Extruded Food Products and Additives (FUNEXFOOD)" (HRZZ-1321) financed by the Croatian Research Foundation, a laboratory single-screw extruder has been modified so it can operate both in classical conditions and with supercritical CO_2 (**Figure 1**). Supercritical CO_2 can be added in two places: in front of the die and at the middle section of the compression zone. The addition of supercritical CO_2 before the die only influences the surface – the products are smoother and lighter, while placement in the compression zone also influences the porosity of extrudates.

At present, the research on the influence of supercritical CO_2 extrusion on the retention of phenolics and fibre, the reduction of acrylamide formation and starch damage, and the increase of resistant starch content in snack products and modified flours with the addition of different food industry by-products (defatted cakes of industrial hemp, pumpkin, chestnut, camelina) is in progress.

3. CONCLUSION

Although it is showing great potential for application in the food industry, extrusion with supercritical CO_2 requires additional scientific and professional research before its practical application. Issues regarding expansion still have to be resolved, since expanded products are very easily deflated and the cost-benefit relation should be addressed with regard to the design process with cost-effective functionality.

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HATZ News

REPORT ON THE ACTIVITIES OF THE CROATIAN ACADEMY OF ENGINEERING IN 2016

According to the Statute of the Croatian Academy of Engineering, the Academy, established in 1993, is a scientific organisation of distinguished and prominent scientists in the field of technological and biotechnological sciences with the objective of promoting the sciences, encouraging co-operation of and bringing together the scientists of various technological, biotechnological and other professions in order to support efficient scientific and economic development of Croatia without gaining any profit.

In 2009, the Academy was recognised as a scientific organisation by the Ministry of Science, Education, and Sports of the Republic of Croatia.

Since 2000, the Academy has been a member of the CAETS (International Council of Academies of Engineering and Technological Sciences), and, since 2005, a member of the Euro-CASE (European Council of Academies of Applied Sciences, Technologies and Engineering).

In 2016, the representatives of the Academy, Prof. Vladimir Andročec, PhD, President of the Academy, and Prof. Zdravko Terze, PhD, Vice-President of the Academy, have attended two meetings of the Euro-CASE Board as the Board Members. The first meeting took place in May 2016 in Paris, France, and the second, in November 2016 in Lyngby, Denmark.

The Academy representatives have also participated in the meetings concerning the SAPEA Project (Science Advice for Policy by European Academies), on which our Academy is engaged through its Euro-CASE membership. The Project is very interesting for the academic community as well as for the economy and political life of the EU Member Countries. It has been conceived by the European Commission and serves to represent inter-academy co-operation at the EU level. It encompasses five associations of the European academies (The Five European Academy Networks): AE - Academia Europaea, ALLEA – All European Academies, EASAC – European Academies Science Advisory Council, Euro-CASE – European Council of Academies of Applied Sciences, Technologies and Engineering, and FEAM – Federation of European Academies of Medicine. Aside from the European academies this Project also brings together the academies from Israel, Armenia, Georgia, and Turkey. The goal of this inter-academy co-operation at the EU level is to provide the European Commission with an independent and interdisciplinary science-based policy by virtue of combining resources of 100 individual academies across Europe, with hundreds of members each and covering all scientific disciplines: social sciences, humanities, natural sciences, engineering sciences and biomedical sciences. The SAPEA Project was officially launched on December 13, 2016, in Bruxelles and is funded within the Horizon 2020 Programme.

Through its memberships both in CAETS and Euro-CASE our Academy is also engaged at the "EU–US Frontiers of Engineering" Platform. The Platform is organised by the US National Academy of Engineering, the largest and the most influential CAETS Member Academy. Following the extensive preparations during 2016, the 2017 Symposium "EU-US Frontiers of Engineering" will take place on November 16-18, 2017 at the University of California in Davis, CA, US. The Symposium is organised jointly by the CAETS (NAE) and Euro-CASE Member Academies (TAF – Technology Academy Finland) and will be dedicated to the development, challenges, and co-operation between the EU and the US in the field of engineering.

The representatives of the Academy Prof. Vladimir Andročec, PhD and Prof. Zdravko Terze, PhD, have participated at the 2016 Euro-CASE Annual Conference "Big Data – Smarter Products, Better Societies", which was held on November 13-15, 2016 in Lyngby, Denmark.

The Croatian Academy of Engineering, through its Euro-CA-SE membership, is also engaged in the Engineering Education Platform, dedicated to a stronger positioning and visibility of the engineering education within a wider corpus of the European Commission's policies, which are dedicated to higher education in Europe and directly connected to research and development as the preconditions for the creation of new jobs, economic growth and prosperity of the EU.

In 2016 the Academy has been patron and co-organiser of 14 distinguished international and domestic scientific and profe-

ssional meetings as well as organiser of 15 meetings, and it participated in 50 meetings of public interest. Among the most important meetings is the 2nd Croatian Engineers' Day, organised by the Croatian Engineering Association (HIS), Croatian Academy of Engineering and Faculty of Electrical Engineering and Computing in Zagreb (FER), was held on March 2, 2016, at FER in Zagreb.

On October 17, 2016, the Academy has organised the Ceremony of Unveiling of the Bust of Prof. Vatroslav Lopašić, PhD, distinguished Croatian physicist and late Honorary Member of the Academy. The bust is the work of art by a distinguished Croatian academic sculptor Boris Leiner.

The publishing activity of the Academy in 2016 has been abundant. The Academy has published one new issue of its Bulletin in Croatian, the "Tehničke znanosti" Vol. 20(1) 2016 as well as two new issues of its Bulletin in English, the "Engineering Power" Vol. 11(1) 2016 and Vol. 11(2) 2016, the later issue of which has been dedicated to the first Croatian Nobel Prize Winner Prof. Leopold Ružička, PhD, following the 40th Anniversary of his death.

The Academy has also published the "Annual 2015 of the Croatian Academy of Engineering", encompassing the reprints of the best scientific papers by its members, which had been previously published in the most prominent international scientific journals. The reprints were published in the "Annual" with permissions of both the original publishers and authors of the papers.

In co-operation with the Public Open University Zagreb, the Academy was the patron and co-publisher of the monograph by Prof. Gojko Nikolić, PhD, "The Life and Inventions of Faust Vrančić" – The Second Extended and Updated Edition.

In 2016 the Academy had held numerous meetings of its bodies: 20 Governing Board meetings, 3 Presidency meetings, 1 Assembly meeting and many meetings of Departments, Standing Committees and Centres.

In 2016 the Academy had issued and conducted the Internal Call for the Election of New Members of the Academy and New Emeriti of the Academy. Eight new Emeriti of the Academy have been elected as well as thirteen new Members of the Academy. Seven scientific and higher-education institutions, organisations, and companies have been elected to Supporting Members of the Academy.

In the same year, the Academy had issued and conducted the Call for Applications for the Awards of the Academy for the year 2015. The 2015 Award for Lifetime Achievement and the Medal of the Academy has been granted to Prof. Emer. Zlatko Kniewald, PhD, retired Professor Emeritus and Full Professor with Tenure of the University of Zagreb at the Faculty of Food Technology and Biotechnology, Emeritus of the Academy in the Department of Bioprocess Engineering, Secretary of the Department and Member of the Presidency of the Academy,

who had also served as the President of the Academy for two terms: 2003-2005 and 2005-2009. The 2015 Rikard Podhorsky Annual Awards have been granted to Prof. Bojan Jerbić, PhD, Full Professor of the University of Zagreb at the Faculty of Mechanical Engineering and Naval Architecture, Member of the Academy in the Department of Systems and Cybernetics, Secretary of the Department and Member of the Presidency of the Academy, and to Prof. Damir Ježek, PhD, Full Professor of the University of Zagreb at the Faculty of Food Technology and Biotechnology, Dean of the Faculty, Member of the Academy in the Department of Bioprocess Engineering. The 2015 Vera Johanides Awards for Young Scientists have been granted to: Tomislav Capuder, PhD, University of Zagreb, Faculty of Electrical Engineering and Computing, Tomislav Pukšec, PhD, University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture, Ana Belščak-Cvitanović, PhD, University of Zagreb, Faculty of Food Technology and Biotechnology, and Ivan Marović, PhD, University of Rijeka, Faculty of Civil Engineering.

Our Academy has a particularly successful co-operation with the Croatian Academy of Sciences and Arts, the leading Croatian scientific and cultural institution. The two Academies have signed the Agreement on Co-operation in 2014. A very successful co-operation has also been realised with both the Croatian Academy of Sciences and Arts and the Miroslav Krleža Institute of Lexicography in the joint project of Croatian Technical and Technological Encyclopaedia. The tri-partite Protocol on Co-operation on the Project of Croatian Technical and Technological Encyclopaedia has been signed in 2014. The intensive work of all parties on this project during the previous years, and especially in 2016, will result in the publishing of the first volume of the Encyclopaedia in 2017. On our Academy's part, members of the Academy nominated by the Science Council of the Academy as authors and editors, have been particularly engaged on this very important and valuable project.

In the previous year, the Academy has also been engaged in an excellent co-operation with its sister academies in the Republic of Croatia: Croatian Academy of Medical Sciences, Croatian Academy of Legal Sciences and Croatian Academy of Forestry Sciences. The quadrilateral Agreement on Co-operation between our four Academies has been signed in 2012 and ever since the Academies co-operate and engage on a number of successful joint activities and projects, meetings, lectures and fora. We would like to especially highlight the joint Scientific Symposium of the four Academies, "Modern Technologies: The Ethics of Utilisation and the Legal Regulation" initiated by the Croatian Academy of Medical Sciences, which was held on March 17, 2017, at the Croatian Physicians' Assembly in Zagreb, Croatia, and vas very successful. The four Academies co-operate through the Council and Co-ordination of the Academies, which serve as their organisational and co-ordinative bodies.

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