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Characterization of pore structure of rice grits extrudates using mercury intrusion porosimetry, nitrogen adsorption and water vapour desorption methods

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ABSTRACT

Rice grits with different moisture contents (10, 15, 20, and 30%, db) were processed by extrusion cooking in a single-screw extruder. Porosity of the extruded products was analyzed respectively using three different methods: water vapour desorption (WVD), nitrogen adsorption (NA) and mercury intrusion porosimetry (MIP). Pore size distribution was determined in the range of pore radius 1–50 nm (WVD), 1–100 nm (NA) and 3.6–7500 nm (MIP). Extrusion cooking resulted in samples of various porosities. The lowest cumulative pore volume (CPV) determined by NA and MIP and the lowest specific surface area calculated on basis of NA and WVD data were noted for the sample produced at 30% feed moisture content. Pore size distribution curves plotted on the base of MIP showed that the end-products of extrusion were characterized by more diverse porosity in the range of smaller radius (5–50 nm) than rice grits.

1. Introduction

Extrusion cooking is commonly applied to manufacture pre-cooked cereal products and a wide range of ready-to-eat foods. They are nowadays more and more popular due to their convenience of consumption, ease of preparation and storage, as well as appearance, taste and texture which are attractive for the consumers. Extrusion cooking is a high-temperature short-time (HTST) process, since cooking temperature can be as high as 180–190 °C during extrusion, but retention time is usually only 20–40 s (Zhuang et al., 2010). Extrusion uses a combination of a few parameters: pressure, shear, moisture, and heat. For the production of expanded cereals products, this technique usually requires moisture content less than 25%, most commonly 13%–17% (Bhattacharya, 2012). There is also another area of extrusion which utilizes higher moisture levels for production of unconventional food products ("wet extrusion") (Akdogan, 1999). Although it seems to be uncomplicated technology, in reality it is difficult to be controlled. Parameters such as type and composition of raw material, type of extruder, extruder screw speed, feed water content, barrel temperature and temperature profile, feed rate affect end-product. The effects of extrusion parameters on structural changes and product properties of rice-based materials have been extensively studied by several authors (Bryant et al., 2001; Kadan et al., 2003; Sacchetti et al., 2004; Singh et al., 2007; Zhuang et al., 2010).

Porosity, pore size and pore size distribution (PSD) are important parameters characterizing texture as well as diffusional and mechanical properties of food materials (Karathanos and Saravacos, 1993). They also affect sensory attributes such as crispness of snack foods (Dogan and Kokini, 2007). According to IUPAC (Sing et al., 1985) pores in solid materials can be classified into three groups: a) macropores (width > 50 nm), b) mesopores (2 nm < width < 50 nm), c) micropores (width < 2 nm). The micropores have also two subgroups: ultramicropores (width < 0.7 nm) and supermicropores (0.7 nm < width< 2 nm). A full description of pore size distribution (pore structure) across a wide range of pore sizes is not possible using one method. The most frequently applied methods for determination of extrudate

Abbreviations: APD, average pore diameter; CPV, cumulative pore volume; FMC, feed moisture content; NA, nitrogen adsorption; MIP, mercury intrusion porosimetry; PSD, differential pore size distribution; p/p_o, relative pressure; S_{BET}, specific surface area determined by BET method; TP, total porosity; WVD, water vapour desorption.

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porosity are nitrogen adsorption (Włodarczyk-Stasiak and Jamroz, 2008; Włodarczyk-Stasiak et al., 2014; Sokolowska et al., 2013), water vapour sorption (Jamroz et al., 1999b; Włodarczyk-Stasiak and Jamroz, 2008), SEM (Rzedzicki and Błaszczak, 2005), TEM (Voyle, 1987), SAXS (Jamroz and Pikus, 1997), X-ray microtomography (XMT) (Babin et al., 2007; Chaunier et al., 2007; Chanvrier et al., 2014), helium pycnometry (Gautam and Choudhury, 1999) as well as mercury intrusion porosimetry (Juppo et al., 1997; Jamroz et al., 1999a, Skiba et al., 2008).

In the methods based on the phenomenon of physical adsorption on the boundary of the gaseous phase usually adsorption isotherms of nitrogen, argon, krypton or water vapour are determined. They are followed by calculating the monolayer capacity based on the BET adsorption isotherm (Brunauer et al., 1938; Sokolowska, 2011). Nitrogen adsorption allows to define the porosity of a material in a whole range of mesopores and lower range of macropores (pore diameters 1.7–300 nm). Mercury intrusion porosimetry is useful in the case of meso- and macroporous adsorbents. With this method, pores between about 500 μm and 3.5 nm in diameter can be investigated and information regarding pore size distribution, total pore volume or porosity, skeletal and apparent density and specific surface area of a sample can be obtained (Ościk, 1982; Giesche, 2006). Both above described methods require advanced equipment, whereas the water vapour sorption can be measured at room temperature with the use of a simple vacuum chamber method. Water vapour (at 23–25 °C) can penetrate pores of smaller sizes than it is possible with the application of nitrogen adsorption (Naono and Hakuman, 1993).

The objective of this work was the application of three different methods for the investigation of internal porosity of rice grits extrudates in relation to moisture content.

2. Materials and methods

2.1. Samples

Rice grits from commercial rice (Sigma) was used as a raw material. It contained approximately 80% of starch, 8.1% of protein and 0.9% of lipids.

2.2. Extrusion-cooking process

Industrial single-screw cooker S-45 (Metalchem Gliwice, Poland) with a barrel length/screw diameter ratio of 12 and a screw compression ratio 3:1 was used for extrusion-cooking (specifications described by Mościcki, 1994). Prior to the process, samples of the rice grits were equilibrated overnight to four feed moisture levels (db): 10, 15, 20 and 30%. The samples were fed into the extruder at a constant feed rate (20 kg h^{-1}) using a volumetric feeder. Extrusion-cooking was carried out at the temperature ranged 110–160–145 °C (in the first zone, second zone, and forming die) with constant 80 rpm screw speed. The die had a 4 mm diameter. The barrel and screw die temperature, as well as the screw speed were monitored from a control panel. Table 1 presents in details the applied process parameters. Steady state extrusion conditions, indicated by steady state temperature and torque, were reached after 15 min. The steady-state samples were then collected and dried in air. Extruded products (Extr 1- Extr 4) were produced in duplicate and used for the further analyses. Unprocessed rice grits containing approximately 10% moisture served as a control sample.

2.3. Expansion ratio

The expansion ratio was defined as the ratio of the extrudate and die diameters. Each mean was an average of ten estimations. The diameters of the air-dried extrudates (room temperature, moisture content approximate 10%) were determined with a vernier caliper with the 0.05 mm precision.

2.4. Bulk density

The density (ρ) was derived using the formula

$$\rho = w\cdot\left(\pi r^2 l\right)^{-1} \tag{1}$$

with r, l and w being the stick radius, length and weight, respectively. Ten estimations (in $g\cdot cm^{-3}$) were made on the extrudate sticks.

2.5. Shearing stress

Shearing stress ($N\cdot cm^{-2}$) was calculated as the extrudate shear force to the cross-section area ratio. Instron 4302 instrument was used for determination of the extrudate texture (6–6.5% of moisture, dry basis) in ten replicates.

2.6. Solid phase density

Samples of extrudates were ground and dried at 105 °C. Solid phase density of the samples were determined using a helium pycnometer Ultrapycnometr 1000 (Quantochrome, Boynton Beach, FL). A chamber containing the sample was filled with spectrally pure helium and closed. Solid phase density was calculated from the volume of helium that was pumped inside the sample and the sample mass.

2.7. Water vapour adsorption and desorption

Pores of equivalent radius 0.05–0.001 μm were determined on the basis of water vapour desorption isotherms according to Naono and Hakuman (1993). The samples were air-dried, ground in a laboratory coffee mill and passed through a 0.2 mm sieve. Only the aggregates less than 0.2 mm were used for the determination. The measurements were done on 2 g samples in three replicates. The isotherms were measured using the vacuum chamber method at a temperature T = 294 ± 0.1 K (Sokołowska, 2004a). The relative

Table 1
Characteristics of extrudates from rice grits and extrusion process conditions.

Sample	FMC (%)	Temperature profile (°C)	Die opening (mm)	Screw speed (rpm)	Feed rate (kg h^{-1})	Bulk density (g cm^{-3})	Expansion ratio	Shearing stress (N cm^{-2})
Extr 1	10	110–160–145	4	80	20	0.72 ± 0.07[*a]	4.20 ± 0.14[a]	16.83 ± 2.53[a]
Extr 2	15	110–160–145	4	80	20	0.89 ± 0.05[b]	3.68 ± 0.25[b]	25.20 ± 5.38[b]
Extr 3	20	110–160–145	4	80	20	1.29 ± 0.10[c]	2.46 ± 0.22[c]	37.92 ± 6.00[c]
Extr 4	30	110–160–145	4	80	20	1.82 ± 0.08[d]	1.65 ± 0.35[d]	96.27 ± 15.80[d]

[*] Standard deviation.
[a-d] Samples with different letters in the same column are significantly different at $P < 0.05$.