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Characteristics of rapeseed oil cake using nitrogen adsorption

Z. Sokołowska[1], G. Bowanko[1], P. Boguta[1], J. Tys[1], and K. Skiba[2]*

[1]Institute of Agrophysics, Polish Academy of Sciences, Doświadczalna 4, 20-290 Lublin, Poland
[2]Polish Patent Office, Niepodległości 188/192, 00-950 Warsaw, P.O. Box 203, Poland

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A b s t r a c t. Adsorption of nitrogen on the rapeseed oil cake and rapeseed oil cake with wheat meal extrudates was investigated. The results are presented as adsorption-desorption isotherms. The Brunauer-Emmet and Teller equation was used to analyse the experimental sorption data. To obtain estimates of the surface area and surface fractal dimension, the sorption isotherms were analyzed using the Brunauer-Emmet and Teller and Frenkel-Halsey-Hill equations. Mesopore analysis was carried out using the Dollimore and Heal method. The properties and surface characteristic of rapeseed oil cake extrudates are related to different basic properties of particular samples and duration of the extrusion process. Extrusion conditions lead to essential differences in particular products. For all kinds of rapeseed oil cakes the amount of adsorbed nitrogen was different, but for the rapeseed oil cake extrudates a large amount of adsorbed nitrogen was observed. The average surface area of the rapeseed oil cake extrudates was about 6.5-7.0 $m^2 g^{-1}$, whereas it was equal to about 4.0-6.0 $m^2 g^{-1}$ for rapeseed oil cake with the wheat meal extrudates. In the case of non-extruded rapeseed oil cake and wheat meal, the dominant group included *ca*. 2 and 5 nm pores. The values of surface fractal dimension suggested that the surface of the extrudates was more homogenous than that of the raw material. Duration of the extrusion process to 80 s resulted in a decrease in the specific surface area, surface fractal dimension, and porosity of the extrudates.

K e y w o r d s: rapeseed oil cake extrudates, nitrogen sorption, specific surface area, fractal dimension, porosity

INTRODUCTION

Physical gas adsorption is often used as a method to study the surface and pore characteristics of solid materials. The technique accurately determines the amount of a gas retained by a solid body, which is a direct measure for the surface and porous properties. The method is relatively fast and relatively easy in operating the equipment. The isotherm obtained from experiments can provide information about the surface area, surface energetic and geometric heterogeneity, pore volume and pore size distribution (PSD). Nitrogen adsorption at 77 K is a standard method for investigation of porous solids and can be used for routine quality control, as well as for investigation of new materials (Rouquerol *et al*., 1994; Sing, 2001).

The theory of fractals is becoming more and more widely used for describing the structure of disordered media and the processes occurring in them (Senesi and Wilkinson, 2008). Many methods have been developed to obtain surface fractal dimensions (D_s) of adsorbents on the basis of different experiments. Among those, the methods based on analysis of adsorption isotherms play an important role, since they require only one complete adsorption isotherm for a given adsorbent to calculate the surface fractal dimension (Terzyk *et al*., 2003). A simple method for calculation of the fractal dimension from a single adsorption isotherm was developed by Jaroniec (1995).

Many investigators have attempted to measure surface area as a means of better description of the solid body under study or better understanding particular processes or reactions. The usual method for determining the surface area of textured solids is based on the adsorption of gases or vapours, and on the application of the Brunauer-Emmet and Teller (BET) equation (Gregg and Sing, 1978).

Rapeseed processing in the food and chemical industry results in some by-products which can be used as animal feeds or as a protein component of the diet (Lomascolo *et al*., 2012). The content of residual oil left after rapeseed processing is around 35% for rapeseed, around 5 to 10% for rapeseed cake, and 1 to 2% for rapeseed meal. Rapeseed

*Corresponding author e-mail: zosia@maja.ipan.lublin.pl

cake is a source of energy but its use in animal feeds is limited by antinutrative substances (Männer, 2001; Thiyam *et al*., 2006). The harmful effects of these antinutritive substances may be reduced by the extrusion process (Kraugerud and Svihus, 2011). During extrusion cooking, raw materials undergo various chemical and structural transformations. Additionally, the product quality can vary considerably depending on the extrude type, screw configuration, feed moisture, temperature profile in the barrel, and screw speed (Arhaliass *et al*., 2009; Oluwole *et al*., 2013; Włodarczyk-Stasiak *et al*., 2009; Stasiak *et al*., 2012). Tarathanos and Saravacos (1993) found that gelatinized starches have average pore sizes of 0.8-1.5 μm and bulk porosity lower than 0.1 cm^3 g^{-1}. High porosity and large pores resulted when starch was extruded at high temperatures. Extruded starches had pores varying from 1 to 120 μm and bulk porosity from 0.1 to 0.95 cm^3 g^{-1}. Fortuna *et al*. (2000) report correlations between the specific surface area, mesopore volume of starch, and certain parameters of gelatinization characteristics.

The objective of this work was to investigate adsorption/desorption of nitrogen on rapeseed oil cake and its mixture with wheat meal. The isotherms were used to determine porosity, the surface fractal dimension and the specific surface area of rapeseed oil cake and its mixtures.

MATERIALS AND METHODS

The materials investigated included rapeseed oil cake and its 50/50 mixtures with wheat meal. The samples were labelled as follows: symbols RSC1 and RSC2 denote rapeseed oil cakes extruded during 40 and 80 s, respectively. Symbols RSWC1 and RSWC2 stand for, respectively, for rapeseed oil cake with wheat meal, the former extruded during 40 s and 80 s. Non-extruded rapeseed oil cake (RSC) was used as a reference sample. The rapeseed oil cake, a by-product from the Polish Oil Industry 'Bielmar' (in Bielsko Biała), was obtained from a winter variety of rapeseed (Bolko). Commercial wheat flour (Polish Standard: PN-91/a-74022) was used. The chemical composition of the material was described in details by Skiba *et al*. (2008). The feed samples were processed by extrusion cooking in a twin-screw extruder type 2S 9/5 (Z.M.Ch. Metalchem Gliwice, Poland). Extrudates (produced by the Faculty of Process Engineering, Agricultural University in Lublin) were prepared in barothermal conditions (barrel temperature up to 130- 160°C, feed moisture 10%, die opening 4 mm), but at different times of processing – 40 and 80 s.

The adsorption isotherms of nitrogen at 80 K were obtained using Sorptomatic 1999 made by Fisons apparatus. Before adsorption measurement the samples were dried at 105°C and outgassed. The measurements for each sample were replicated three times. We have estimated that the precision of all the measurements was better than 0.5% and the greatest errors were observed at the highest relative pressures.

The surface area of the extrudates was evaluated from adsorption isotherms in the BET range of relative nitrogen pressure ($0<p\,p_0^{-1}<0.35$), using the Brunauer-Emmett-Teller (BET) method (Gregg and Sing, 1978). The experimental data were modelled using the BET equation.

The first step in the application of the BET method is to obtain the monolayer capacity (N_m) from the BET plot at a lineal range of water vapour pressure $0<p\,p_0^{-1}<0.35$. The second step is to calculate the surface area S from the dependence:

$$S = N_m M^{-1} \mathrm{L}\varpi, \quad (1)$$

where: L is the Avogadro number (6.02 10^{23} molecules per mole), M is the molecular weight of nitrogen (in gram per mole) and ϖ is the molecule cross-sectional area (16.4 10^{-20} m^2 for a nitrogen molecule).

The Frenkel-Halsey-Hill (FHH) isotherm was originally developed to describe the growth of a thick film on a flat surface and to analyze the wetting phenomena. It was next extended to the case of adsorption on fractal surfaces (Terzyk *et al*., 2003).

The nitrogen sorption data were also used to estimate the surface fractal dimensions by the method based on the Frenkel-Hill-Halsey (FHH) equation. According to this approach the isotherm is approximated using the Eq. (2) (Jaroniec, 1995; Jarzębski *et al*., 1997):

$$\ln N = -(1/m)\ln(-\ln(x)) + \mathrm{C}, \quad (2)$$

where: C is a constant and the parameter m is related to the surface fractal dimension of the sample. The FHH approach yields a straight line and allows evaluation of the fractal dimension from its slope ($-1/m$). If the adsorption occurs according to the van der Waals mechanism, the fractal dimension is equal to: $D_s=3(1-1/m)$. However, if the adsorption is governed by the capillary condensation mechanism, $D_s=3-1/m$.

Mesopore analysis was carried out using the Dollimore and Heal method (DH) (Dollimore and Heal, 1964). This method is applied in the range of relative pressure >0.35, assuming cylindrical geometry for the pores. In the DH method, the surface of the adsorption layer in pores emptied during subsequent stages of desorption is a result of pore surface and the ratio of corresponding Kelvin radii of pores emptied at the nth stage to the mean effective radii of pores emptied at the nth stage. The calculation was made on the basis of the desorption isotherm using the data – relative pressure, from which the corresponding volume of adsorbate and the thickness of the adsorbed layer were determined.

The adsorption isotherms, specific surface area and porosities were calculated using the program Maillstone 100, which is the software developed for Sorptomatic 1999.

RESULTS AND DISCUSSION

Figure 1 shows the experimental adsorption isotherms for rapeseed oil cake (RSC), rapeseed oil cake extrudates (RSC1, RSC2), and rapeseed oil cake with wheat meal extrudates (RSWC1, RSWC2). In general, the shape of adsorption curves is similar. According to the BET classification of the adsorption isotherms (Gregg and Sing, 1978), all the curves belong to the same class, namely to type II, which describes physical adsorption and is closely linked with multi-layer structure formation. However, the detailed course of the curves and the amount of adsorbed nitrogen vary from sample to sample. The lowest nitrogen adsorption is found on natural rapeseed oil cake. For samples RSC1 and RSC2, the amount of adsorbed nitrogen increases. When the wheat meal was added to rapeseed oil cake, the amount of adsorbed nitrogen decreased. The differences between the amounts of adsorbed nitrogen on the materials investigated are more visible at higher relative pressure of nitrogen.

A hysteresis effect in adsorption and desorption isotherms is observed for all the samples investigated. Figure 2 shows an example of the hysteresis loop obtained for samples RSC, RSC2, and RSWC2. Samples RSC2 and RSW1 possess relatively large hysteresis loops. The remaining samples exhibit similar, but smaller loops. The hysteresis loops begin at relative pressure about 0.4. As it was reported by Sing (2001), in the case of nitrogen at 77 K, the hysteresis closure point is never bellow $p\ p_0^{-1}$~0.4, which corresponds to the lower limit of capillary condensation hysteresis. The hysteresis loop corresponds to type H3 according to the IUPAC classification (Gregg and Sing, 1978). This type of a hysteresis loop is usually associated with the capillary condensation in a mesoporous structure (Gregg and Sing, 1978; Sing, 2001) and with the change in the material porosity during the adsorption-desorption process (Skiba *et al*., 2008; Włodarczyk-Stasiak and Jamroz, 2009).

The adsorption data were used to evaluate the values of the specific surface area (*S*). The experimental data were described using the BET equation. The high values of the correlation coefficient (R^2) indicate that the BET equation provides a good fit to the experimental data for $0<p\ p_0^{-1}<0.35$. In all the cases, the values of R^2 varied from 0.987 to 0.997. For the samples under study the average BET specific surface area ranged from 4.3 to about 7 $m^2 g^{-1}$. Generally, the specific surface areas of the extrudates were greater than the natural rapeseed oil cake (5.6 $m^2\ g^{-1}$). In addition, for rapeseed oil cake extrudates RSC1 and RSC2 the values of *S* were generally higher than for extrudates RSWC1 and RSWC2. The value of the specific surface area of extrudates is connected with the extrusion time. Duration of the extrusion process up to 80 s resulted in a decrease in the specific surface area. The reduction of the *S* value is more visible for the mixture of the rapeseed oil cake and the wheat meal. A comparison of the *S* values of extrudate RSWC1 (6.3 $m^2\ g^{-1}$) and RSWC2 (4.3 $m^2\ g^{-1}$) with the *S* value of the non-extruded mix- ture of the rapeseed oil cake and the wheat meal (5.1 $m^2\ g^{-1}$) confirms the effect of extrusion time on the value of the specific surface area.

Extrusion conditions cause essential differences in the surface area and also in the porosity of particular products. The DH method allows determination of the average specific pore volume at the relative pressure 0.998, the

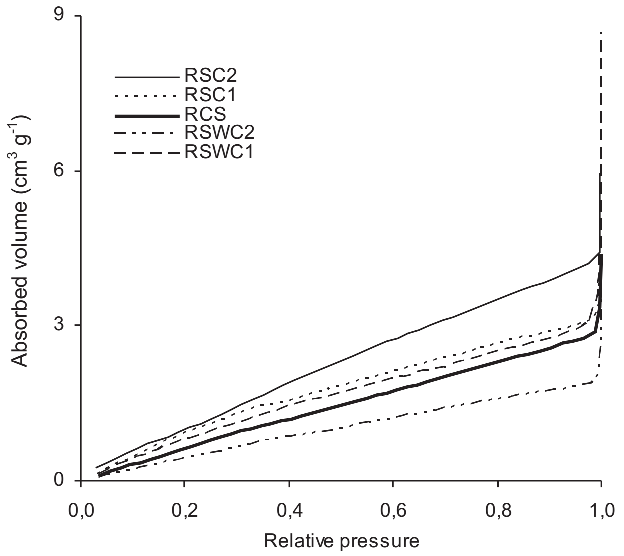

Fig. 1. Adsorption isotherms of nitrogen on the rapeseed oil cake and its mixtures with the wheat meal. Abbreviations: see in the text.

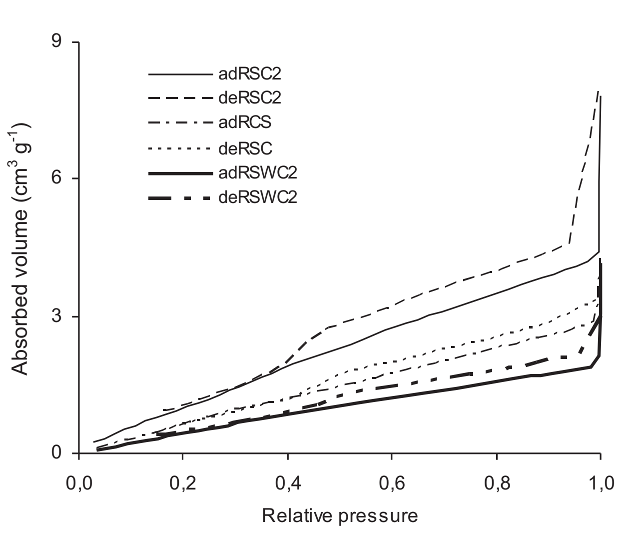

Fig. 2. Hysteresis loop for rapeseed oil cake and its mixtures with wheat meal. Abbreviations: see in the text.

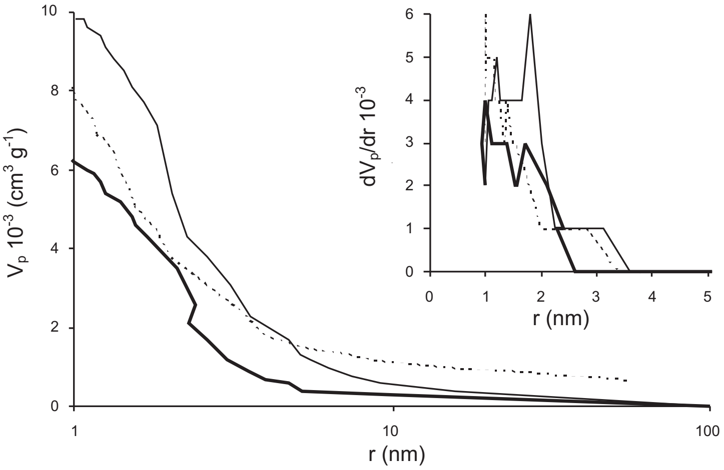

Fig. 3. Cumulative pore volume (V_p) and differential pore size distribution (PSD) functions versus pore radius for rapeseed oil cake materials.

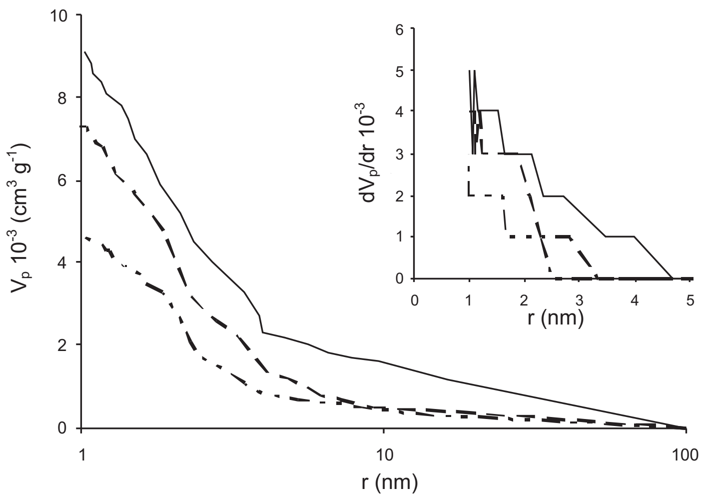

Fig. 4. Cumulative pore volume (V_p) and differential pore size distribution (PSD) functions versus pore radius for rapeseed oil cake +wheat meal extrudate.

cumulative pore volume (V_p), and the pore size distribution (PSD) for rapeseed oil cake materials (Fig. 3), and for rapeseed oil cake+wheat meal extrudate (Fig. 4).

The average specific V_p varies from 4.60 10^{-3} to 8.88 10^{-3}cm^3 g^{-1}. Duration of the extrusion process up to 80 s results in a decrease in the specific pore volume for extrudate RSWC2 , while for extrudate RSC2 the V_p increases.

The curves of the cumulative pore volume (Figs 3 and 4) for the extrudates investigated and non-extruded rapeseed oil investigated possess a similar shape and all of them are situated between the curves for non-extruded rapeseed oil cake and wheat meal. They indicate that the greatest number of pores in the range of 1-100 nm radii is found for extrudate RSC2, while the lowest one – for extrudate RSWC2. The materials extruded during 40 s exhibit a similar number of pores in the range of 1-100 nm. The values of the mesopore pore volume obtained by the DH method (V_{DH}) vary from 4.4 to 9.7 cm^3 g^{-1}, whereas the average specific pore volume (V_p) at the relative pressure 0.998 from 4.60 10^{-3} to 8.88 10^{-3} cm^3 g^{-1}. The pore volumes V_p and V_{DH} are very similar and the correlation coefficient R^2 between them is 0.699. This suggest that the number of macropores is rather small. The effect of extrusion conditions is more visible for rapeseed oil material. In comparison to the non-extruded rapeseed oil cake, extrudates RSC1, RSWC1 and RSC2 exhibit higher values of $V_{DH,}$ while the materials extruded for 40 s display no difference in V_{DH}. The prolongation of the extrusion process up to 80 s results in an increase in V_{DH} for RSC2 and a decrease in V_p for RSWC2.

Figures 3 and 4 also present the differential pore size distribution (PSD) functions versus pore radius. Plots of PSD for rapeseed oil cake materials are similar in shape (Fig. 3); plots for wheat meal, RSWC1 and RSWC2 are also similar (Fig. 4). A group of pores of 1-3.5 nm radii is found in extrudates RSC1, RSC2, RSWC1, and RSWC2, while in the case of non-extruded rapeseed oil cake and wheat meal, the

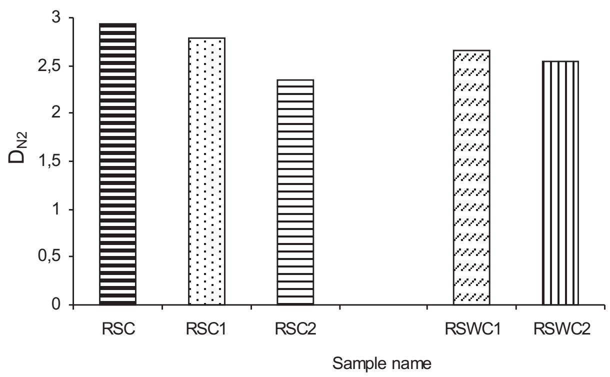

Fig. 5. Surface fractal dimension (D_{N2}) for investigated materials

dominant group includes *ca*. 2 and 5 nm wide pores. Generally, the maximum peaks appear at about 1-2 nm, which corresponds to 6 10^{-3}cm^3 g^{-1} pore volume for extrudates RSC1 and RSC2 and to 3-4 10^{-3} cm^3 g^{-1} pore volume for extrudates RSWC1 and RSCW2. The effect of extrusion conditions is similar as for V_{DH}. Skiba *et al.* (2008) found significant changes in porosity under the effect of the extrusion process for pores with radii lager than about a dozen micrometers.

The difference in pore characteristics observed for the rapessed oil cake extrudates and rapessed oil cake+wheat meal extrudates is connected with the presence of the wheat meal. Wheat meal was reported to require high temperature to achieve a significant expansion and reduced density during extrusion cooking (Qing-Bo Ding *et al*., 2006). A mercury porosimetry study of the wheat flour extrudate (Jamroz *et al*., 1999) showed that the total pore volume of wheat extrudate was lower than for raw material. Moreover, Skiba *et al*. (2008) found that the extrudate mixture of rapeseed oil cake and wheat meal (mixture 50/50) was characterized by a considerable decrease in porosity compared to the rapeseed oil cake alone.

For the description of such complex structures as those found in a majority of porous solids, the fractal geometry has emerged as an analytical tool (Rouquerol *et al*., 1994). Additionally, quantitative description of the surface roughness of foods has been achieved by a application of the concept of fractal dimension (Mazurkiewicz, 2011; Pedreschi *et al*., 2000; Smoczyński *et al*., 1999).

The surface fractal dimension (D_{N2}) of the materials investigated varies from 2.33 to 2.67 (Fig. 5). For RSC and RSWC1 the surface fractal dimension is 2.61 and 2.67, respectively, which indicates clearly that surfaces of these samples are geometrically heterogeneous. Prolongation of the extrusion process up to 80 s results in a decrease in the value of the surface fractal dimension, and for extrudates RSWC2 and RSC2 the value of D_{N2} is 2.33 and 2.36, respectively. Lower values of the surface fractal dimension imply that the surface of these extrudates are 'smoother' than the former materials. A positive correlation was found between the surface fractal dimension, D_{N2}, and the content of the fiber in extrudates was found (R varied from 0.854 to 0.95). The fibre content was provided by Skiba *et al*. (2008).

CONCLUSIONS

1. The specific surface areas of the extrudates are greater than of the natural rapeseed oil cake. Reduction of the specific surface value is particularly visible for the mixture of the rapeseed oil cake and the wheat meal. Prolongation of the extrusion process up to 80 s causes a decrease in the specific surface area of the extrudates.

2. The average specific pore volume at the relative pressure 0.998 varies from 4.60 10^{-3} to 8.88 10^{-3} cm^3 g^{-1}. A group of pores of 1-4 nm radii in was found in the extrudates.

3. The differences in pore characteristics of the rapessed oil cake extrudates and rapeseed oil cake+wheat meal extrudates were related to the presence of the wheat meal and duration of the extrusion process.

4. The surface fractal dimension (D_{N2}) of the materials investigated varies from 2.33 to 2.67 and decreases with an increase in the time of extrusion. The increase in the processing time yields smoother surfaces.

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