

REVIEW MODELS OF SORPTION ISOTHERMS PREGLED MODELA SORPCIONIH IZOTERMI

Vangelce MITREVSKI*, Cvetanka MITREVSKA**, Ljupco TRAJCEVSKI*, Borce MITREVSKI***

*Faculty of Technical Sciences, Bitola, Makedonska Falanga 33, North Macedonia

**Faculty for Safety Engineering, Sveti Nikole, North Macedonia

***Center for Energy Efficiency "Bobi Turs", Bitola, North Macedonia

e-mail: vangelce.mitrevski@uklo.edu.mk

ABSTRACT

Numerous mathematical models for approximation of sorption data of food and agriculture materials are available in the referent scientific and engineering literature. Depending on the number of parameters included in the model for approximation of moisture sorption data, the models may be one, two, three, four, five or more parametric. Also the sorption models may be included or not the temperature as a parameter into the equation. The objectives of the presented article was a review of one hundred seventy-two sorption no temperature dependent sorption isotherm models which used to for approximation equilibrium moisture data of food materials. For statistics evaluation of those models the equilibrium moisture data of quince were used. The value on coefficient of determination the root mean squared error, the mean relative deviation and graphical evaluation of the residual randomness were the main assessment criterions for statistical evaluation of the sorption isotherms model. Based on the performed statistical analysis it was concluded that the model of Popovski&Mitrevski i.e. M161 has the best statistical performances.

Key words: models of sorption isotherms, statistical evaluation, quince.

REZIME

Krive sorpcije i desorpcije su veoma važne pri definisanju ravnotežne vlažnosti prehrambenih i poljoprivrednih proizvoda. Predviđanje promena ovih veličina u zavisnosti od stanja okolnog vazduha su veoma važne za procese sušenja i skladištenja. Za aproksimaciju sorpcionih podataka prehrambenih materijala u referentnoj naučnoj i inženjerskoj literaturi dostupni su brojni matematički modeli. Zavisno od broja parametara, modeli mogu biti jedno, dvo, tro, četvero, peto ili više parametarski. Sa druge strane, ovi modeli mogu biti zavisni ili nezavisni od temperature okolnog vazduha. U radu je prikazana statistička ocena sto sedamdeset i dva temperaturno nezavisnih sorpcionih modela koji su korišćeni za aproksimaciju ravnotežne vlažnosti dunje. Na osnovu dobijenih rezultata može se zaključiti da model Popovski & Mitrevski t.e. model sa referentnim brojem M161 ima najbolje statističke performanse. Glavni kriterijumi statističke ocene bili su koeficijent determinacije, kvadratni koren srednje kvadratne greške, srednja relativna devijacija kako i grafička prezentacija slučajnih ostataka regresione analize. Vrednosti statističkih parametara modela Popovski & Mitrevski procenjene su salaganjem sa eksperimentalnim podacima ravnotežne vlažnosti dunje sa procenjenim vrednostima dobijenim korišćenjem Quasi-Newton metodom procene koji minimizira greške sume kvadrata.

Ključne reči: modeli izoterma sorpcije, statistička ocena, dunja.

INTRODUCTION

In the reference scientific and engineering literature in the last few years have an increasing number of articles in which was research sorption isotherm problems of food materials. These articles includes the methods for determination of sorption or desorption isotherms (Mitrevski et al., 2015; Mitrevski et al., 2018), temperature dependence of sorption isotherms (Popovski&Mitrevski, 2004), determination of heat of sorption and development of mathematical models for approximation of moisture sorption data (Mitrevski et al., 2012; Mitrevski et al., 2015a). In the previously article (Mitrevski et al., 2019, Mitrevski et al., 2020) it was concluded that in depending on the number of parameters which are included in the mathematical model for approximation of moisture sorption data, the models may be one, two, three, four, five or more parametric. The objectives of the presented article is a review of sorption isotherm models and statistical evaluation of one hundred seventy two sorption isotherm models for approximation of equilibrium moisture data. The statistically performance of those models were tested on the equilibrium moisture data of quince. From the performed statistical analyze it was concluded that the model of Popovski&Mitrevski i.e. the model M161 (Popovski&Mitrevski, 2005), has the best statistical performances.

NOMENCLATURE:

A, B, C, D, E	- parameters
a_w (-)	- water activity
MRD (-)	- mean relative deviation
R^2 (-)	- coefficient of determination
RMSE (-)	- the root mean squared error
X_{eq} (kg/kg)	- equilibrium moisture content

MATERIAL AND METHODS

The equilibrium moisture content of quince was determined at temperatures of 15, 30, 45 and 60°C using static gravimetric method (Mitrevski et al., 2018). Ten saturated salt solutions L_iCl , CH_3COOK , $MgCl$, K_2CO_3 , $Mg(NO_3)_2$, $NaBr$, $SrCl_2$, $NaCl$, KCl and $BaCl_2$ were used to give defined constant equilibrium relative humidity in the glass jars from 0.110 to 0.920 (Mitrevski et al., 2018). Three replications were made at each temperature and equilibrium relative humidity in the glass jars, using two samples per replication, and the average values of the equilibrium moisture content were calculated (Mitrevski et al., 2019).

RESULTS AND DISCUSSION

The experimental values for the equilibrium moisture content, X_{eq} on the slices of the quince at each water activity, a_w for the four different temperatures (Mitreviski et al., 2018) were fitted with one hundred seventy two sorption isotherm models M01-M172, presented in tab.1 to tab.5.

Table 1. A one parameter sorption isotherm models

Num. model	Name of model	Model	References
M01	de Boer	$X_{eq} = \frac{A}{1-a_w}$	de Boer, 1953
M02	Tester	$X_{eq} = \frac{Aa_w}{1-a_w}$	Tester, 1956

Table 2. A two parameters sorption isotherm models

Num. model	Name of model	Model	References
M03	BET modified	$X_{eq} = \frac{ABa_w}{[(1-a_w)(1-B\ln(1-a_w))]}$	Al-Muhtaseb et al., 2004
M04	Bradley	$X_{eq} = A\ln(-\ln a_w) + B$	Bradley, 1936
M05	Brunauer	$X_{eq} = \frac{Aa_w}{(1-a_w)(1-Ba_w)}$	Brunauer et al., 1938
M06	Caurie ≡ Miniowitsch	$X_{eq} = \exp(Aa_w + B)$	Caurie, 1970
M07	Chen and Clayton ≡ Bradley (for T=const)	$X_{eq} = A\ln(-\ln a_w) + B$	Chen and Clayton, 1971
M08	Chung and Pfof ≡ Bradley (for T=const)	$X_{eq} = A\ln(-\ln a_w) + B$	Chung and Pfof, 1967
M09	Chung-Pfof	$X_{eq} = A + B(\ln a_w)$	Chung and Pfof, 1967
M10	Day and Nelson ≡ Henderson (for T = const)	$X_{eq} = A\ln[-\ln(1-a_w)] + B$	van den Berg and Bruin, 1981
M11	Dubinin and Radushkevich	$X_{eq} = \exp[A\ln(a_w^2)]B$	Dubinin and Radushkevich, 1947
M12	Freundlich ≡ McGavack and Patrick	$X_{eq} = Ba_w^A$	Freundlich, 1926
M13	Halsey	$X_{eq} = A(-\ln a_w)^B$	Halsey, 1948
M14	Halsey modified	$X_{eq} = A + B\left(\frac{a_w}{1-Ba_w}\right)$	Iglesias and Chirife, 1981
M15	Harkins and Jura	$X_{eq} = \sqrt{\frac{A}{B-\ln a_w}}$	Jura and and Harkins, 1943
M16	Henderson	$X_{eq} = A[-\ln(1-a_w)]^B$	Henderson, 1952
M17	Hoover-Mellon ≡ Bradley	$X_{eq} = A\ln(-\ln a_w) + B$	van den Berg and Bruin, 1981
M18	Hüttig	$X_{eq} = \frac{Aa_w(1+a_w)}{1-Ba_w}$	Hüttig, 1948
M19	Iglesias and Chirife ≡ Halsey (for T=const)	$X_{eq} = B(-\ln a_w)^A$	Iglesias and Chirife, 1976
M20	Iglesias and Chirife	$X_{eq} = A + \frac{Ba_w}{1-a_w}$	Iglesias and Chirife, 1981

M21	Isse	$X_{eq} = \exp[\ln(\frac{A}{1-a_w}) + B]$	Isse et al., 1993
M22	Kühn	$X_{eq} = A + B/\ln a_w$	Kuhn, 1964
M23	Langumir	$X_{eq} = \frac{Aa_w}{1-Ba_w}$	Langumir, 1918
M24	Linear equation	$X_{eq} = A + Ba_w$	Castillo et al., 2003
M25	McGavac and Partric	$X_{eq} = Aa_w^B$	McGavack and Partric, 1920
M26	Miniowitsch	$X_{eq} = \exp(Aa_w + B)$	Lykow, 1958
M27	Mizrahi	$X_{eq} = \frac{A}{1-a_w} + B$	Mizrahi et al., 1970
M28	Mizrahi modified	$X_{eq} = A\frac{a_w}{1-a_w} + B\frac{1}{1-a_w}$	Castillo et al., 2003
M29	Oswin	$X_{eq} = A\left(\frac{a_w}{1-a_w}\right)^B$	Oswin, 1946
M30	Pierce	$X_{eq} = A\ln(1-a_w) + B$	Pierce and Inst, 1929
M31	Polanyi	$X_{eq} = A(-\ln a_w)^{-1/3} + B$	Polanyi, 1928
M32	Popovski and Mitrevski	$X_{eq} = \frac{Aa_w}{(1-Ba_w)^2}$	Popovski and Mitrevski, 2003
M33	Popovski and Mitrevski	$X_{eq} = A\ln[-\ln(1-a_w)] + B$	Popovski and Mitrevski, 2006
M34	Popovski and Mitrevski	$X_{eq} = A\ln\frac{a_w}{1-a_w} + B$	Popovski and Mitrevski, 2006
M35	Popovski and Mitrevski	$X_{eq} = \frac{A\sin a_w}{1-a_w} + B$	Popovski and Mitrevski, 2007
M36	Popovski and Mitrevski	$X_{eq} = \frac{A\cos a_w}{\sin(1-a_w)} + B$	Popovski and Mitrevski, 2007
M37	Popovski and Mitrevski	$X_{eq} = \frac{Atga_w}{1-a_w} + B$	Popovski and Mitrevski, 2007
M38	Popovski and Mitrevski	$X_{eq} = \exp\left[\frac{A}{\sin a_w} + B\right]$	Popovski and Mitrevski, 2007
M39	Popovski and Mitrevski	$X_{eq} = \exp\left[\frac{A\sin(1-a_w)}{a_w} + B\right]$	Popovski and Mitrevski, 2007
M40	Popovski and Mitrevski	$X_{eq} = \exp\left(\frac{A}{tga_w} + B\right)$	Popovski and Mitrevski, 2007
M41	Popovski and Mitrevski	$X_{eq} = \frac{1}{\frac{A}{\sin a_w} + B}$	Popovski and Mitrevski, 2007
M42	Popovski and Mitrevski	$X_{eq} = \frac{a_w}{A\sin(1-a_w) + Ba_w}$	Popovski and Mitrevski, 2007
M43	Popovski and Mitrevski	$X_{eq} = \frac{1}{\frac{A}{tga_w} + B}$	Popovski and Mitrevski, 2007
M44	Popovski and Mitrevski	$X_{eq} = A\left(\frac{\sin a_w}{1-a_w}\right)^B$	Popovski and Mitrevski, 2007
M45	Popovski and Mitrevski	$X_{eq} = A\text{tg}^B a_w$	Popovski and Mitrevski, 2007
M46	Popovski and Mitrevski	$X_{eq} = A\left(\frac{tga_w}{1-a_w}\right)^B$	Popovski and Mitrevski, 2007
M47	Popovski and Mitrevski	$X_{eq} = \frac{A}{\arcsin(1-a_w)} + B$	Popovski and Mitrevski, 2007
M48	Popovski and Mitrevski	$X_{eq} = \frac{A}{\arccos a_w} + B$	Popovski and Mitrevski, 2007
M49	Popovski and Mitrevski	$X_{eq} = \frac{Aa_w}{\arctg a_w} + B$	Popovski and Mitrevski, 2007
M50	Popovski and Mitrevski	$X_{eq} = \exp\left(\frac{A}{\arcsin a_w} + B\right)$	Popovski and Mitrevski, 2007
M51	Popovski and Mitrevski	$X_{eq} = \exp\left(\frac{A}{\arctg a_w} + B\right)$	Popovski and Mitrevski, 2007
M52	Popovski and Mitrevski	$X_{eq} = \exp\left[\frac{\text{Arctg}(1-a_w)}{a_w} + B\right]$	Popovski and Mitrevski, 2007

M53	Popovski and Mitrevski	$X_{eq} = \frac{1}{\frac{A}{\arcsin a_w} + B}$	Popovski and Mitrevski, 2007
M54	Popovski and Mitrevski	$X_{eq} = \frac{1}{\frac{A}{\arctg a_w} + B}$	Popovski and Mitrevski, 2007
M55	Popovski and Mitrevski	$X_{eq} = \frac{a_w}{A \arctg \dots (1-a_w) + Ba_w}$	Popovski and Mitrevski, 2007
M56	Popovski and Mitrevski	$X_{eq} = A \arcsin^B a_w$	Popovski and Mitrevski, 2007
M57	Popovski and Mitrevski	$X_{eq} = A \left(\frac{a_w}{\arccos a_w}\right)^B$	Popovski and Mitrevski, 2007
M58	Popovski and Mitrevski	$X_{eq} = A \left(\frac{a_w}{\arctg a_w}\right)^B$	Popovski and Mitrevski, 2007
M59	Posnow	$X_{eq} = \frac{A}{B - \ln a_w}$	Lykow, 1958
M60	Smith ≡ Pierce	$X_{eq} = A \ln(1 - a_w) + B$	Smith, 1947
M61	Thompson ≡ Henderson (for T=const)	$X_{eq} = A \ln[-\ln(1 - a_w)] + B$	Thompson et al., 1968
M62	White and Eyring	$X_{eq} = \frac{A}{1 - Ba_w}$	White and Eyring, 1947

Table 3. A three parameters sorption isotherm models

Num. model	Name of model	Model	References
M63	Anderson	$X_{eq} = \frac{Aa_w}{(1 - Ba_w)(1 - Ca_w)}$	Anderson, 1946
M64	Brunauer et al.,	$X_{eq} = \frac{[a_w^2(Aa_w - A - 1) + 1]a_w B}{[(Ca_w - C + 1)a_w - 1](a_w - 1)}$	Brunauer et al., 1940
M65	BET modification	$X_{eq} = \frac{ABC a_w}{(1 - Ba_w)(1 - Ba_w) + BC a_w}$	Mohamed et al., 2005
M66	Chen ≡ de Boer - Zwikker	$X_{eq} = B \ln(A - \ln a_w) + C$	Chen, 1971
M67	Chirife et al.	$X_{eq} = \exp[(A + B \ln(a_w^{c-1} - 1))]$	Castillo et al., 2003
M68	Fink and Jackson	$X_{eq} = \exp[(A + B \ln(C - \ln a_w))]$	Fink and Jackson, 1973
M69	de Boer and Zwikker	$X_{eq} = A \ln(B - \ln a_w) + C$	de Boer and Zwikker, 1929
M70	Fontán et al.,	$X_{eq} = \left(\frac{A}{B - \ln a_w}\right)^C$	Fontán et al., 1982
M71	Filonenko and Chuprin	$X_{eq} = 1/(A/a_w + B + Ca_w)$	Filonenko and Chuprin, 1967
M72	Hailwood and Horrobin	$X_{eq} = \frac{A}{1 - Ba_w} + C$	Hailwood and Horrobin, 1946
M73	Haynes	$X_{eq} = B\sqrt{(A - \ln a_w)} + C$	Haynes, 1961
M74	Kats and Kutarov	$X_{eq} = \frac{ABa_w(1 - a_w^*)}{[(1 - a_w)(1 - a_w + Ca_w)]}$	Kats and Kutarov, 1999
M75	Lewicki	$X_{eq} = [A/(1 - a_w)^B - (A/(1 + a_w))]^C$	Lewicki, 2000
M76	Mitrevski	$X_{eq} = \exp(A + B \ln a_w + C \ln^2 a_w)$	Mitrevski et al., 2015a
M77	Mitrevski	$X_{eq} = \exp\left[A + \frac{B}{1 + a_w} + \frac{C}{(1 + a_w)^2}\right]$	Mitrevski et al., 2015a
M78	Mitrevski	$X_{eq} = \exp\left[A + B \frac{1 + a_w}{1 + 2a_w} + C \left(\frac{1 + a_w}{1 + 2a_w}\right)^2\right]$	Mitrevski et al., 2015a
M79	Mitrevski	$X_{eq} = \exp(A + B \exp a_w + C \exp^2 a_w)$	Mitrevski et al., 2015a
M80	Mitrevski	$X_{eq} = \exp[A + B \exp(1 - a_w) + C \exp^2(1 - a_w)]$	Mitrevski et al., 2015a
M81	Mitrevski	$X_{eq} = \exp[A + B \ln(1 + a_w) + C \ln^2(1 + a_w)]$	Mitrevski et al., 2015a
M82	Mitrevski	$X_{eq} = \exp\left[A + B \frac{a_w}{\ln(1 + a_w)} + C \left[\frac{a_w}{\ln(1 + a_w)}\right]^2\right]$	Mitrevski et al., 2015a

M83	Mitrevski	$X_{eq} = \exp\left[A + B \frac{a_w}{\sin a_w} + C \left(\frac{a_w}{\sin a_w}\right)^2\right]$	Mitrevski et al., 2015a
M84	Mitrevski	$X_{eq} = \exp\left[A + B \frac{\sin a_w}{a_w} + C \left(\frac{\sin a_w}{a_w}\right)^2\right]$	Mitrevski et al., 2015a
M85	Mitrevski	$X_{eq} = \exp\left[A + B \frac{\arcsin a_w}{a_w} + C \left(\frac{\arcsin a_w}{a_w}\right)^2\right]$	Mitrevski et al., 2015a
M86	Mitrevski	$X_{eq} = \exp\left[A + B \frac{a_w}{\arctan a_w} + C \left(\frac{a_w}{\arctan a_w}\right)^2\right]$	Mitrevski et al., 2015a
M87	Pickett	$X_{eq} = \frac{(A^B - 1)a_w}{(a_w - 1)(Ba_w + C)}$	Pickett, 1945
M88	Polinomial equation	$X_{eq} = A + Ba_w + Ca_w^2$	Castillo et al., 2003
M89	Popovski and Mitrevski	$X_{eq} = [A \ln(-\ln a_w) + B]^C$	Popovski and Mitrevski, 2004b
M90	Popovski and Mitrevski	$X_{eq} = \left[\frac{Aa_w}{(1 - a_w)(1 - Ba_w)}\right]^C$	Popovski and Mitrevski, 2004b
M91	Popovski and Mitrevski	$X_{eq} = \left[\frac{Aa_w(1 + a_w)}{1 - Ba_w}\right]^C$	Popovski and Mitrevski, 2004b
M92	Popovski and Mitrevski	$X_{eq} = \left(\frac{Aa_w}{1 - Ba_w}\right)^C$	Popovski and Mitrevski, 2004b
M93	Popovski and Mitrevski	$X_{eq} = \left(\frac{A}{1 - a_w} + B\right)^C$	Popovski and Mitrevski, 2004b
M94	Popovski and Mitrevski	$X_{eq} = [A \ln(1 - a_w) + B]^C$	Popovski and Mitrevski, 2004b
M95	Popovski and Mitrevski	$X_{eq} = \left[\frac{Aa_w}{(1 - Ba_w)^2}\right]^C$	Popovski and Mitrevski, 2004b
M96	Popovski and Mitrevski	$X_{eq} = (Aa_w^2 + B)^C$	Popovski and Mitrevski, 2004b
M97	Popovski and Mitrevski	$X_{eq} = \left(\frac{A}{1 - Ba_w}\right)^C$	Popovski and Mitrevski, 2004b
M98	Popovski and Mitrevski	$X_{eq} = \frac{Aa_w}{(1 - a_w)(1 - Ba_w)} + C$	Popovski and Mitrevski, 2005
M99	Popovski and Mitrevski	$X_{eq} = A[-\ln(1 - a_w)]^B + C$	Popovski and Mitrevski, 2005
M100	Popovski and Mitrevski	$X_{eq} = \frac{Aa_w(1 + a_w)}{1 - Ba_w} + C$	Popovski and Mitrevski, 2005
M101	Popovski and Mitrevski	$X_{eq} = A(1 - a_w)^B + C$	Popovski and Mitrevski, 2005
M102	Popovski and Mitrevski	$X_{eq} = Ae^{Ba_w} + C$	Popovski and Mitrevski, 2005
M103	Popovski and Mitrevski	$X_{eq} = Aa_w^B + C$	Popovski and Mitrevski, 2005
M104	Popovski and Mitrevski	$X_{eq} = A\left(\frac{a_w}{1 - a_w}\right)^B + C$	Popovski and Mitrevski, 2005
M105	Popovski and Mitrevski	$X_{eq} = \frac{Aa_w}{(1 - Ba_w)^2} + C$	Popovski and Mitrevski, 2005
M106	Popovski and Mitrevski	$X_{eq} = \frac{A}{B - \ln a_w} + C$	Popovski and Mitrevski, 2005
M107	Popovski and Mitrevski	$X_{eq} = \frac{Aa_w^2}{(1 - Ba_w)(1 - Ca_w)}$	Popovski and Mitrevski, 2005a
M108	Popovski and Mitrevski	$X_{eq} = \frac{Aa_w^2(1 + a_w)}{(1 - Ba_w)(1 - Ca_w)}$	Popovski and Mitrevski, 2005a
M109	Popovski and Mitrevski	$X_{eq} = \left(\frac{A}{1 - a_w} + B\right) \frac{a_w}{1 - Ca_w}$	Popovski and Mitrevski, 2005a
M110	Popovski and Mitrevski	$X_{eq} = Aa_w^B e^{Ca_w}$	Popovski and Mitrevski, 2005a
M111	Popovski and Mitrevski	$X_{eq} = Aa_w^B (1 - a_w)^C$	Popovski and Mitrevski, 2005a
M112	Popovski and Mitrevski	$X_{eq} = \frac{Aa_w^B}{(1 - Ca_w)^2}$	Popovski and Mitrevski, 2005a
M113	Popovski and Mitrevski	$X_{eq} = Ae^{Ba_w} \left(\frac{a_w}{1 - a_w}\right)^C$	Popovski and Mitrevski, 2005a
M114	Popovski and Mitrevski	$X_{eq} = A(-\ln a_w) B [-\ln(1 - a_w)]^C$	Popovski and Mitrevski, 2005a

M115	Popovski and Mitrevski	$X_{eq} = \frac{A}{(B - \ln a_w)(C - \ln a_w)}$	Popovski and Mitrevski, 2005a
M116	Popovski and Mitrevski	$X_{eq} = \frac{A}{(1-a_w)^2} + \frac{B}{1-a_w} + C$	Popovski and Mitrevski, 2005a
M117	Popovski and Mitrevski	$X_{eq} = (\frac{A}{1-Ba_w} + C) \frac{a_w}{1-a_w}$	Popovski and Mitrevski, 2005b
M118	Popovski and Mitrevski	$X_{eq} = (\frac{A}{1-Ba_w} + \frac{C}{1-a_w})a_w$	Popovski and Mitrevski, 2005b
M119	Popovski and Mitrevski	$X_{eq} = \frac{Aa_w}{1-a_w} + \frac{B}{1-Ca_w}$	Popovski and Mitrevski, 2005b
M120	Popovski and Mitrevski	$X_{eq} = a_w [\frac{A(1+a_w)}{1-Ba_w} + \frac{C}{1-a_w}]$	Popovski and Mitrevski, 2005b
M121	Popovski and Mitrevski	$X_{eq} = \exp(\frac{A}{1-Ba_w} + C)$	Popovski and Mitrevski, 2006
M122	Popovski and Mitrevski	$X_{eq} = \exp[A(-\ln a_w)^B + C]$	Popovski and Mitrevski, 2006
M123	Rounsley ≡ Pickett	$X_{eq} = \frac{(a_w^A - 1)a_w}{(a_w - 1)(Ba_w + C)}$	Rounsley, 1961
M124	Schuchmann-Roy-Peleg	$X_{eq} = \frac{Aa_w}{(1 + Ba_w)(C - a_w)}$	Schuchmann et al., 1990
M125	Tóth	$X_{eq} = \frac{Aa_w}{(a_w^B + C)^{\frac{1}{n}}}$	Tóth, 1971
M126	Young and Nelson	$X_{eq} = A[\frac{a_w(1-B)}{a_w + (1-a_w)B} + \frac{B^2}{B-1} \ln(1 - (1-1/B)a_w) - (B-1) \ln(1-a_w)] + C(a_w^2/a_w + (1-a_w)B)$	Castillo et al., 2003

Table 4. A four parameters sorption isotherm models

Num. model	Name of model	Model	References
M127	Enderby	$X_{eq} = a_w (\frac{A}{1-Ba_w} + \frac{C}{1-Da_w})$	Enderby, 1955
M128	Kollmann	$X_{eq} = Aa_w^n + \exp[(a_w - C)^2 D]$	Kollmann, 1962
M129	McLaren & Rowen	$X_{eq} = \frac{a_w}{1-a_w} (\frac{A}{1-Ba_w} + \frac{C}{1-Da_w})$	McLaren & Rowen, 1951
M130	Peleg	$X_{eq} = Aa_w^B + Ca_w^D$	Peleg, 1993
M131	Polynomial equation	$X_{eq} = A + Ba_w + Ca_w^2 + Da_w^3$	Castillo et al., 2003
M132	Popovski & Mitrevski	$X_{eq} = \exp(Aa_w)B + \exp(Ca_w)D$	Popovski and Mitrevski, 2004a
M133	Popovski & Mitrevski	$X_{eq} = A(\frac{a_w}{1-a_w})^B + C(\frac{a_w}{1-a_w})^D$	Popovski and Mitrevski, 2004a
M134	Popovski & Mitrevski	$X_{eq} = \exp[A \ln(a_w)^2 B + \exp(C \ln(a_w)^2) D]$	Popovski and Mitrevski, 2004a
M135	Popovski & Mitrevski	$X_{eq} = \frac{A}{(1-Ba_w)} + \frac{C}{(1-Da_w)}$	Popovski and Mitrevski, 2004a
M136	Popovski & Mitrevski	$X_{eq} = A(-\ln a_w)^B + C(-\ln a_w)^D$	Popovski and Mitrevski, 2004a
M137	Popovski & Mitrevski	$X_{eq} = a_w(1+a_w) + (\frac{1}{1-Ba_w} + \frac{C}{1-Da_w})$	Popovski and Mitrevski, 2004a
M138	Popovski & Mitrevski	$X_{eq} = A[-\ln(1-a_w)]^B + C[-\ln(1-a_w)]^D$	Popovski and Mitrevski, 2004a
M139	Popovski & Mitrevski	$X_{eq} = \frac{A}{B - \ln a_w} + \frac{C}{D - \ln a_w}$	Popovski and Mitrevski, 2004a
M140	Popovski & Mitrevski	$X_{eq} = \frac{A}{(1-a_w)^B} + \frac{C}{(1-a_w)^D}$	Popovski and Mitrevski, 2004b
M141	Popovski & Mitrevski	$X_{eq} = a_w [\frac{A}{(1-Ba_w)^2} + \frac{C}{(1-Da_w)^2}]$	Popovski and Mitrevski, 2004b
M142	Popovski & Mitrevski	$X_{eq} = [\frac{Aa_w}{(1-Ba_w)(1-Ca_w)}]^D$	Popovski and Mitrevski, 2004b
M143	Popovski & Mitrevski	$X_{eq} = [\frac{A}{1-Ba_w} + C]^D$	Popovski and Mitrevski, 2004b
M144	Popovski & Mitrevski	$X_{eq} = [\frac{A}{1-Ba_w} + Ca_w]^D$	Popovski and Mitrevski, 2004b

M145	Popovski & Mitrevski	$X_{eq} = \frac{Aa_w(1-a_w^B)}{(1-a_w)(1-Ca_w)} + D$	Popovski and Mitrevski, 2005
M146	Popovski & Mitrevski	$X_{eq} = \frac{Aa_w}{(1-Ba_w)(1-Ca_w)} + D$	Popovski and Mitrevski, 2005
M147	Popovski & Mitrevski	$X_{eq} = (\frac{A}{B - \ln a_w})^C + D$	Popovski and Mitrevski, 2005
M148	Popovski & Mitrevski	$X_{eq} = \frac{A}{1-Ba_w} + Ca_w + D$	Popovski and Mitrevski, 2005
M149	Popovski & Mitrevski	$X_{eq} = \frac{Aa_w^2}{(1-Ba_w)(1-Ca_w)(1-Da_w)}$	Popovski and Mitrevski, 2005a
M150	Popovski & Mitrevski	$X_{eq} = (\frac{A}{1-Ba_w} + C) \frac{a_w}{1-Da_w}$	Popovski and Mitrevski, 2005a
M151	Popovski & Mitrevski	$X_{eq} = a_w [\frac{A}{(1-a_w)(1-Ba_w)} + \frac{C}{1-Da_w}]$	Popovski and Mitrevski, 2005b
M152	Popovski & Mitrevski	$X_{eq} = \frac{Aa_w}{(1-a_w)(1-Ba_w)} + Ca_w^D$	Popovski and Mitrevski, 2005b
M153	Popovski & Mitrevski	$X_{eq} = \frac{Aa_w}{(1-Ba_w)} + Ca_w^D$	Popovski and Mitrevski, 2005b
M154	Popovski & Mitrevski	$X_{eq} = \frac{Aa_w}{(1-Ba_w)} + \frac{C}{(1-Da_w)}$	Popovski and Mitrevski, 2005b
M155	Popovski & Mitrevski	$X_{eq} = a_w [\frac{A(1+a_w)}{(1-Ba_w)} + \frac{C}{(1-Da_w)}]$	Popovski and Mitrevski, 2005b
M156	Popovski & Mitrevski	$X_{eq} = a_w [\frac{A}{(1-Ba_w)(1-Ca_w)} + \frac{D}{(1-a_w)}]$	Popovski and Mitrevski, 2005b
M157	Popovski & Mitrevski	$X_{eq} = \exp(Aa_w^B + Ca_w^D)$	Popovski and Mitrevski, 2006
M158	Riedel	$X_{eq} = \frac{a_w}{(Aa_w + B)} + \frac{Ca_w^D}{(1-a_w)}$	van den Berg, and Bruin, 1981

Table 5. A five parameters sorption isotherm models

Num. model	Name of model	Model	References
M159	D'Arcy-Watt	$X_{eq} = \frac{ABA_w + Ea_w + CDa_w}{1 + Aa_w + Ea_w + CDa_w}$	Saravacos et al., 1986
M160	Popovski-Mitrevski	$X_{eq} = (\frac{A}{1-Ba_w} + \frac{Ca_w}{1-Da_w})a_w + E$	Popovski and Mitrevski, 2005
M161	Popovski-Mitrevski	$X_{eq} = (\frac{A}{1-Ba_w} + \frac{Ca_w}{1-Da_w}) \frac{a_w}{1-a_w} + E$	Popovski and Mitrevski, 2005
M162	Popovski-Mitrevski	$X_{eq} = Aa_w^B + Ca_w^D + E$	Popovski and Mitrevski, 2005
M163	Popovski-Mitrevski	$X_{eq} = Ae^{Ba_w} + Ce^{Da_w} + E$	Popovski and Mitrevski, 2005
M164	Popovski-Mitrevski	$X_{eq} = A(\frac{a_w}{1-a_w})^B + C(\frac{a_w}{1-a_w})^D + E$	Popovski and Mitrevski, 2005
M165	Popovski-Mitrevski	$X_{eq} = Ae^{B \ln^2 a_w} + Ce^{D \ln^2 a_w} + E$	Popovski and Mitrevski, 2005
M166	Popovski-Mitrevski	$X_{eq} = \frac{A}{1-Ba_w} + \frac{C}{1-Da_w} + E$	Popovski and Mitrevski, 2005
M167	Popovski-Mitrevski	$X_{eq} = A(-\ln a_w)^B + C(-\ln a_w)^D + E$	Popovski and Mitrevski, 2005
M168	Popovski-Mitrevski	$X_{eq} = (\frac{A}{1-Ba_w} + \frac{C}{1-Da_w})(1+a_w)a_w + E$	Popovski and Mitrevski, 2005
M169	Popovski-Mitrevski	$X_{eq} = A[(-\ln(1-a_w))^B + C(-\ln(1-a_w))^D] + E$	Popovski and Mitrevski, 2005
M170	Popovski-Mitrevski	$X_{eq} = \frac{A}{B - \ln a_w} + \frac{C}{D - \ln a_w} + E$	Popovski and Mitrevski, 2005
M171	Popovski-Mitrevski	$X_{eq} = A(1-a_w)^B + C(1-a_w)^D + E$	Popovski and Mitrevski, 2005
M172	Popovski-Mitrevski	$X_{eq} = [\frac{A}{(1-Ba_w)^2} + \frac{C}{(1-Da_w)^2}]^{1/n} + E$	Popovski and Mitrevski, 2005
M173	Popovski-Mitrevski	$X_{eq} = \frac{Aa_w}{1-Ba_w} + \frac{Ca_w^D}{1-a_w} + E$	Popovski and Mitrevski, 2005

In this study for the goodness of fit of experimental sorption data and selection of the best sorption isotherm model the coefficient of determination, R², the root mean squared error, RMSE, the mean relative deviation, MRD and graphical evaluation of the residual randomness were used for a statistical indicator for selection of the best sorption isotherm model. The

method of indirect non-linear regression and estimation methods of Quasi-Newton, from computer software Statistica (Statsoft Inc., Tulsa, OK, <http://www.statsoft.com>), were used to approximate the experimental equilibrium moisture content data of quince.

On the basis of experimental data, and each mathematical model from tab. 1 to tab. 5, the values of coefficient of determination, R^2 , were calculated. After that, the models were ranked on the basis of values of the coefficient of determination. In tab. 6 the values of coefficient of determination, the root mean squared error and the mean relative deviation for the best one, two, three, four and five parameters models were presented.

From tab. 6 it is evident that the Popovski&Mitrevski models (M129, M151, 156 and M161) has the highest value of coefficient of determination, $R^2 = 0.9916$ (rank 1). But, the model M161 generated from Popovski and Mitrevski (Popovski&Mitrevski, 2005), has the lowest value of RMS = 0.0274 and MRD = 0.1289. So, this model correlates the experimental values of sorption data of quince better than other

models. The values of model parameters, A, B, C, D and E, for the model of Popovski&Mitrevski i.e. M161 were estimated by fitting the models to experimental equilibrium moisture content data of quince. The estimated values of parameters are given in tab. 7.

Table 6. Statistic summary of the regression analysis

Model	R^2	RMS	MRD	Rank
M02	0.9805	0.0400	0.1600	4
M54	0.9913	0.0276	0.1324	3
M109	0.9914	0.0276	0.1726	2
M117	0.9914	0.0274	0.1354	2
M118	0.9914	0.0274	0.1353	2
M129	0.9916	0.0274	0.1506	1
M151	0.9916	0.0279	0.1363	1
M156	0.9916	0.0274	0.1491	1
M161	0.9916	0.0274	0.1289	1

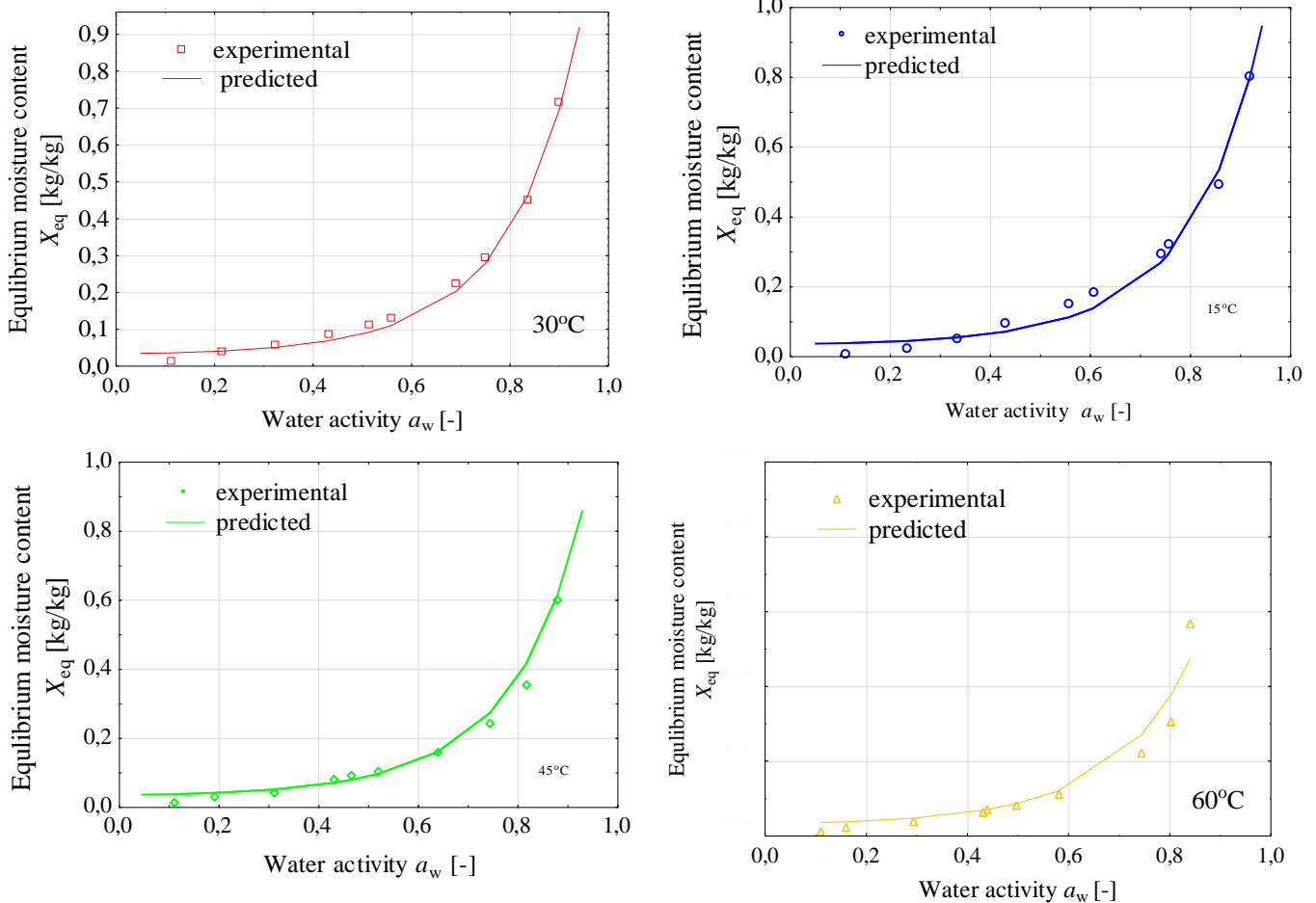


Fig. 1. Experimental and predicted sorption isotherms for quince at 15, 30, 45 and 60 °C for the model M161

Table 7. Estimated values of parameters

Model	A	B	C	D	E
$XEQ = ((A/(1-B*AW))+C/(1-D*AW))*(AW/(1-AW))+E$	0.1372	-0.5734	-0.0005	1.0601	-0.0052

XEQ - equilibrium moisture content, AW- water activity, A, B, C, D, E parameters

The experimental and predicted values for equilibrium moisture content data for quince at four temperatures are shown on fig.1. From fig.1 is evident that has a good agreement between the experimental and predicted values of equilibrium moisture data of quince. From fig.1 is evident that has a good agreement between the experimental and predicted values of equilibrium moisture content data of quince. Analyzing the residues on regression analysis for the model M161, the plots of the residues against the predicted values did not indicate

abnormal distribution. In fig.2 the plots of the residuals of non-linear estimation against the predicted values are presented.

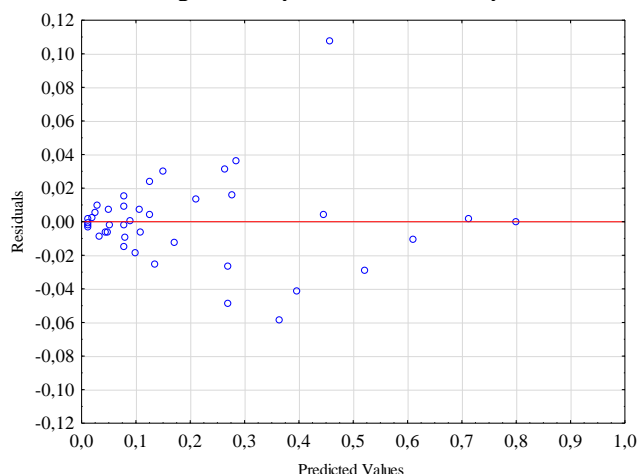


Fig. 2. Residuals plot of sorption data versus predicted values for quince -Model M161

CONCLUSIONS

The experimental equilibrium moisture content data of quince were fitted with one hundred seventy-two sorption no temperature dependent sorption isotherm models. In accordance to proposed statistical criterion it was concluded that the five parameters model of Popovski&Mitrevski i.e. M161, has a better statistical fit on experimental equilibrium moisture data of quince in whole range of water activity than other models.

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