Modeling Approach for the Air Convective Drying of Leafy Materials

A. Orphanides, A. Fantousi, V. Goulas and V. C. Gekas.

Abstract— Mathematical modeling in applied sciences could include predictive approaches in various unit operations of Chemical Engineering and/or Food Engineering. In air convective drying two key factors influence quantitatively and qualitatively the process and the processed material; temperature and air velocity. Although during the drying unit operation a severe shrinkage of leafy material occurs, no explicit account of this fact is taken in herb plant drying modeling. Even more rare, not to say un-existed, are applications of the true driving force, that is the thermodynamic driving force, according to the opinion of the authors. In this work both aspects have been considered and explicitly applied in the modeling of drying of a common herb plant, *Mentha viridis*, used as a model aromatic herb plant material. Furthermore, the study of synergistic or inhibitory effects between the influencing factors is presented. Application of the three before-mentioned aspects leads to interesting findings which are thoroughly discussed in the present paper.

Keywords— Drying, modeling, shrinkage, water activity, multifactorial analysis

I. Introduction

THIS paper carries some new ideas concerning the modeling of the unit operation of drying. In convective air drying two main factors are recognized; temperature and air velocity. Their effects on the quality response parameters concerning the antioxidants contained in the leafy material were studied as well as their interaction effect (synergy or inhibition) through a scheme of a multifunctional design analysis.

Conventional modeling of convective air drying implies the use of the so-called apparent or effective diffusion coefficient, D_{eff}, although the dehydration occurring during the drying process does not follow a strict diffusion mechanism. Application of the above-mentioned coefficient as a predictive tool presents serious difficulties, since reported values of that coefficient in the literature show differences of several orders of magnitude even for the drying of the same species [1], [2].

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Main factors affecting mass transfer during the drying; the shrinkage alters the geometry of the examined specimen and also the driving force, which should not be based on the water content but rather on the water activity in the leafy material and in the air, i.e. the water potential, given that water activity is closely connected to the chemical potential which is also closely connected to energy, according to Thermodynamics [3-5]. Concerning shrinkage, dehydration studies have shown that there is a linear relationship between the volume change ratio and the water content change ratio.

Thus, these two factors are taken explicitly into consideration upon modeling of the drying of leafy materials. To our knowledge, no such study has ever been performed yet. The up-to-date approaches include in the D_{eff} parameter all factors that influence the drying process. The alternative approach, on the contrary, applied in the present paper takes into account both important factors, namely, the shrinkage effect and the true driving force and leads to interesting observations.

II. MATERIALS AND METHODS

A. *Mentha viridis herb*

Fresh *Mentha viridis* leafy material was provided by Agroplant LTD in Limassol, Cyprus, and was used the same day in all experiments carried out in the drying equipment which was the pilot plant air dryer, described below.

A. *Experimental Design*

A complete factorial design was performed, where the independent variables were air temperature (40, 50, 60 and 70°C) and air velocity (1.5, 2, 2.5, 3 m s^{-1}) leading to 16 total of combinations. For each treatment, approximately 100g of fresh, healthy leaves were separated from the stems and subsequently placed in thin layers onto the five trays of the dryer chamber. The weight loss was recorded every 10 sec; the end of drying was defined when the weight remained stable for more than 10 min and the moisture content was lower than 12%. Each experiment was repeated twice and samples were kept at -22°C for further analysis.

B. *The pilot plant air dryer*

The pilot scale air dryer was designed and developed based on previous work [6]. An automatic scale (accuracy ±0.1g) was mounted on top of a flow chamber with controlled temperature and horizontal air flow. A metallic structure comprising of 5 perforated stainless steel trays (allowing the air movement in-between leaves and trays) was hanged by the scale (Fig.1).

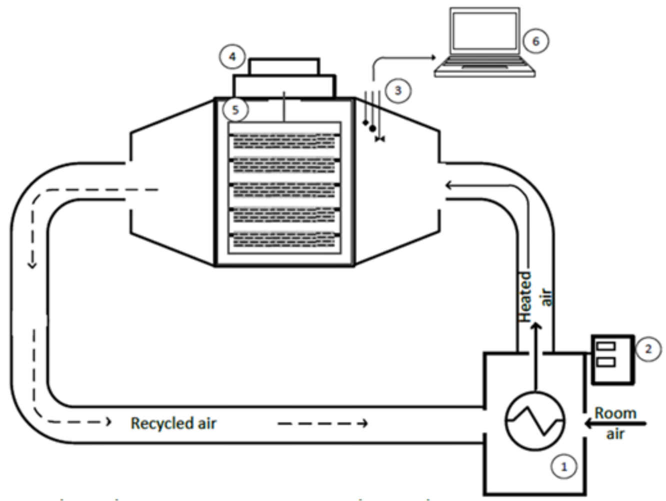

Fig.1 Schematic representation of lab scale air dryer with major parts: 1. Heating Unit; 2. Control Unit; 3. Thermometer, Hygrometer, Anemometer; 4. Electronic Scale; 5. Perforated Stainless Steel Trays; 6. Computer for data recording and processing

D Multifactorial analysis

A method of factorial design analysis provided in the milieu of MATLAB ® has been adapted for the purpose of Food Engineering and Environmental Engineering applications. Its principle was presented in our previous work [7]. A short reminder is given here below:

The level matrix for a two factor scheme is the following:

$$I_2 = \begin{bmatrix} -1 & -1 & 1 \\ 1 & -1 & -1 \\ -1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$$

Low levels and high levels can be defined arbitrarily in the experimental range but convenient. Therefore there are options in the choice of the levels; nevertheless a sensitivity study is recommendable.

Let Y denote one response variable, for example the total phenols contained in the leafy material, whose values at the points of the level combinations of the two-factor are obtained experimentally, and given by the vector Y:

$$Y = [Y1 \quad Y2 \quad Y3 \quad Y4]$$

Then, the three effects of the factors on R are obtained from the vector of the effects:

$$E = [E_A \quad E_B \quad E_{AB}]$$

by the multiplication of the response variable vector times the level matrix for two factors

$$E=[E_A \quad E_B \quad E_{AB}]=[Y1 \quad Y2 \quad Y3 \quad Y4]\cdot I_2$$

E_A being the effect of the factor A, in the present case the direct effect of the temperature, E_B the direct effect of factor B, in our case the air velocity and E_{AB} the combined effect of the two factors , the value of which shows the synergy or the inhibition between the two factors. The synergy (or inhibition term) should be compared to the standard deviation of the experimental values of the response variables in order to conclude about their statistical significance.

E. Analytical methods

The following properties were measured for all combinations of the influencing factors:

- Biophenol contents was determined by spectrophotometric assay [8]. Briefly, 1 mL of diluted extract was mixed with 1 mL of 0.1% HCl-ethanol solution (0.1 mL HCl per 100 mL 95% ethanol) and 8 mL of 2% HCl-Ethanol solution into a 10 mL volumetric flask. The absorbance was measured at 280, 320 and 360 nm using an UV-Vis- spectrophotometer in order to evaluate total phenols, hydroxycinnamates and flavanols, respectively. The corresponding standard curves to the above determinations were prepared using ethanolic solutions of gallic acid (R^2=0.999), caffeic acid (R^2=0.999) and rutin (R^2=0.997), respectively. Results are expressed as mg per g of dry material (d.m). All analyses, including the standard curve were performed in triplicates.
- The measurement of DPPH antioxidant capacity was performed as following: two mL of each extract were mixed with 1 mL solution of DPPH (0.3 mmol L-1). The absorbance of the mixture was measured after 30 min incubation time in the dark at 517 nm. The radical scavenging activity was calculated using a standard curve of 6-hydroxy-2,5,7,8-tetramethyl-chroman-2-carboxylic acid (Trolox) and expressed as mg Trolox 100 g-1 d.m [8].
- Antioxidant capacity was determined according to the ABTS method. The ABTS radical was formed from the reaction of 2.45 mM potassium persulfate with 7 mM ABTS stock solution, kept in the dark and at room temperature for 16 h. Then, ABTS radical was diluted in ethanol until a solution with absorbance of 0.700 ± 0.005 at 734 nm was obtained. A 200 μL aliquot of diluted extract was then homogenized with 1.8 mL of the ABTS radical. Absorbance of the samples was read at 734 nm after 6 min of reaction. Results for three antioxidant activity assays were expressed as μmol Trolox 100 g^{-1} d.m.
- Determination of total antioxidant activity by Ferric Reducing/Antioxidant Power (FRAP) assay was carried out according previous work [8]. A total of 3 mL of freshly prepared FRAP solution (0.3 mol L^{-1} acetate buffer (pH 3.6) containing 10 mmol L^{-1} 2,4,6-tripyridyl-s-triazine and 40 mmol L^{-1} $FeCl_3$•$10H_2O$) were added to 100 μL of extract and were further incubated at 37°C for

4 min; the absorbance at 593nm was measured. Standard solutions of Trolox were used to prepare a standard curve, which was further used to convert the absorbance values into FRAP values, expressed as mg trolox·$100g^{-1}$ d.m.

F. Shrinkage and water activity measurements

The shrinkage ratio was obtained by measuring the dimensions of the leafy material before and after each experiment. The water activity was obtained through the sorption isotherm of the leafy material. The sorption isotherm for 50°C is shown below (Fig.2).

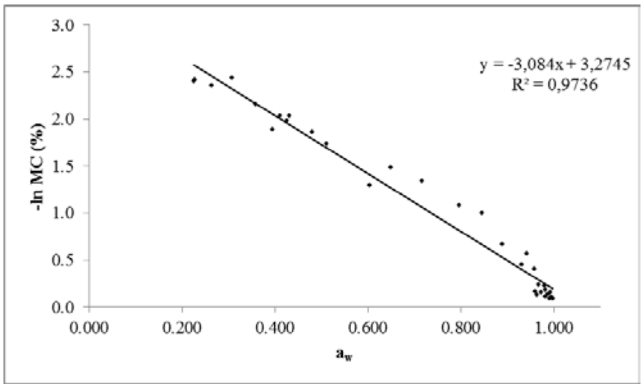

Fig. 2. Sorption Isotherm of *Mentha viridis* at 50°C

III. THEORY

Here the principles of the development of the model are given.

- The leaves are assumed covering uniformly the area through which the water transport takes place.
- The medium in which the transport takes place includes the convective boundary layer attached to the leafy material, thus the leaf layer and the boundary layer are taken as a unit.
- The temperature remains constant during drying thus we refer to isothermal drying.
- The shrinkage is assumed to occur isotropically.
- The driving force for drying is given by the active concentrations/activities rather than simply concentrations. Thus the model belongs to the Thermodynamic models.

In the following the utterly important aspects of shrinkage, the flux and the driving force are considered. Assuming isotropic shrinkage [9], the relationship between water content and volume of the leafy material is as follows:

$$A_t = A_0 \left(\frac{M_t}{M_0}\right)^{2/3} \quad (1)$$

M_0 and M_t being the moisture content the initial one and at time t respectively and A_0 and A_t the surface area, the initial one and at time *t* respectively. The area as a function of the moisture content is introduced in the expression of the mass transfer flux, J

$$J_t = \frac{\Delta M_t}{\Delta t A_t} \quad (2)$$

J_t being the flux at time *t*, during a time interval Δt, ΔM_t is the moisture loss during the interval time Δt, and A_t the surface area of the leafy material to be dehydrated. Thus the effect of shrinkage is explicitly taken into account.

The driving force is modeled as the difference between the water activity in the air (that is the relative humidity of the air) and the water activity in the leafy material of *Mentha viridis*. The relative humidity of the air, ψ, was obtained from registered data in the pilot dryer and the water activity, a_w, of the leafy material was obtained through the sorption isotherm as mentioned above in the Materials and Methods section.

Finally the constitutive equation connecting the flux with the driving force

$$J_t = L_{eff}\left(\alpha_{w_t} - \psi\right) \quad (3)$$

L_{eff} is the thermodynamic mass transfer coefficient, known also as mass conductivity a term coined by G. Crapiste (the Bahia Blanca model) [10].

IV. RESULTS

The results in terms of reduced moisture content versus time for different temperatures at constant air velocity 1.5 m/s, are given in Fig. 3

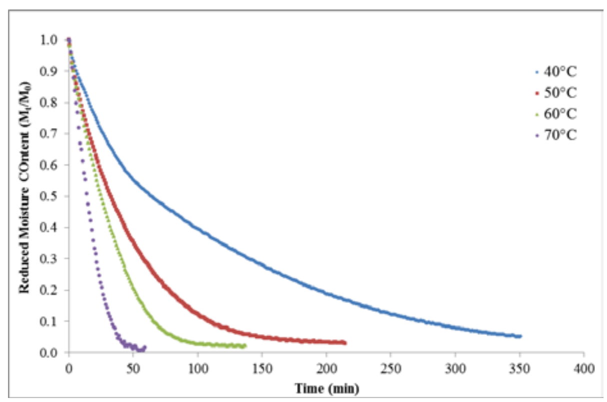

Fig.3. Reduced moisture content vs time at different temperatures for air speed of 1.5 m/s.

Choosing the temperature of 50 °C, for herb quality reasons, the effect of the air velocity on the reduced moisture content is given in Fig.4.

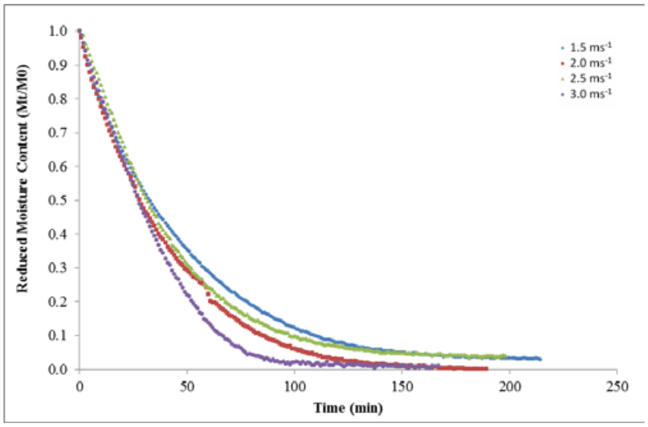

Fig.4. Reduced moisture content vs time at different air velocities for a drying temperature of 50 °C.

Furthermore, plotting the flux vs the driving force as defined above in the section of Theory, straight lines are obtained. An example of such a diagram is shown in Fig.5. This result provides a first strong evidence for the validity of the model developed in this paper.

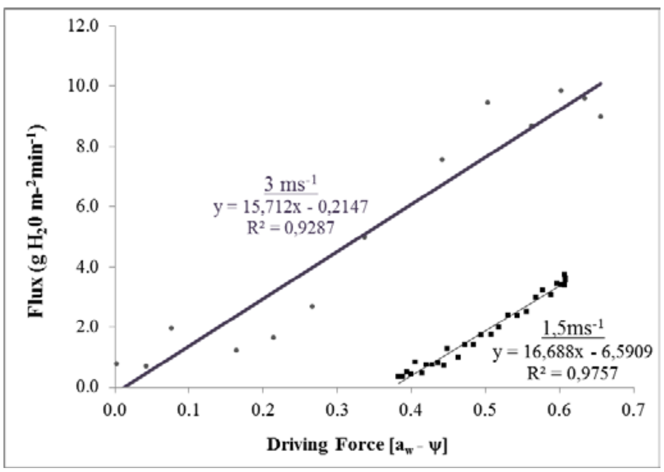

Fig.5 Flux versus driving force for the drying at 50 °C

The results concerning the synergy/inhibition effect between *T*, temperature and *u*, the air velocity on the antioxidant properties of *Mentha viridis* occurring upon drying in different temperature intervals are given in Fig.6, below. In the Y axis is the synergy/inhibition effect , defined as T·u in normalized values, where -1 refers to the eah time taken lower level value of the temperature, respectively +1 refers to the higher level value. .

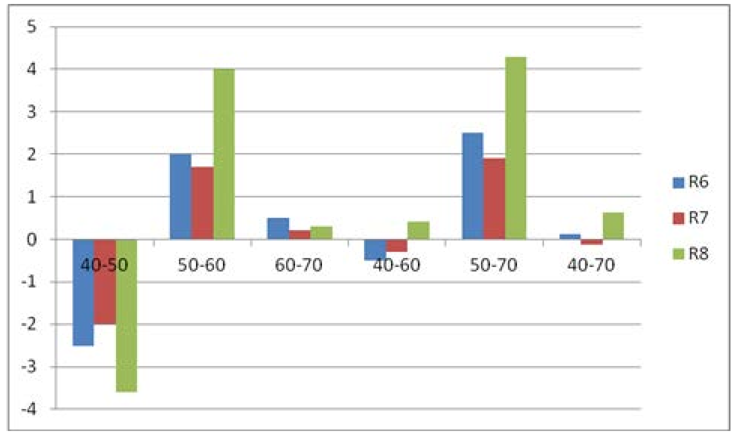

Fig.6 Synergy/inhibition effect on the antioxidant capacity monitored by different methods.

R6 refers to method ABTS, R7 to method DPPH and R8 to method FRAP. In the X axis the temperature intervals are given.

The prevailing pattern of behavior for all methods is very interesting. The multifactorial analysis method is sensitive to the choice of the temperature interval. Synergy/inhibition effects are observed in the two intervals 40-50 °C and 50-60 °C. They are of opposite sign, negative (inhibition) in the 40-50 °C interval and positive (synergy) in the 50 -60 °C interval. In the 40-60 °C interval obviously the two effects are cancelled and the interaction phenomena are negligible. In the next interval 60 to 70 °C the interaction phenomena are also insignificant. As a consequence in the interval 50-70 °C comprising the 50-60 °C interval the profile of the synergy is almost the same as in the 50-60 oC interval. As a consequence also all of the above if we have chosen the interval 40-70 °C from the beginning, not examining what it happens in more detail, we should not obtain the interesting synergy/inhibition effects that we did following our methodology.

V. DISCUSSION

Mathematical modeling is useful in applied Sciences and Engineering, as far as both the primary and the secondary production are concerned [11-12]. In the case studied in the present paper, useful conclusions could be drawn.

Figures 3 and 4 predict a severe shrinkage ration between initial and final values (up to 90% decrease in volume) and this has been verified by the experiment. In the present approach the shrinkage has been taken into account in the water flux. The decrease in the surface leads to an increase of the flux, other things equal, since the surface area *A* is in the denominator of the expression for the flux.

Furthermore, Fig. 5 shows a clear tendency of a phase of increased drying rate for leafy materials, in terms of dehydration flux, opposite to the common establishment of constant and falling rate periods. Of course more experiments are needed to support this interesting finding.

Also Fig. 5 provides strong evidence that the driving force should be based on the water activity than on the moisture content. Thirdly, the L_{eff} (mass conductivity) behaves as a real constant, for the same temperature, compared to the traditionally used D_{eff}.

The results of the multifactorial analysis (Fig. 6) constitute strong challenges to a Food Chemist or Food Biochemist trying to find out what phenomena occur at cell level in the two temperature intervals of 40-50 °C and 50-60°C respectively, which are responsible for the inhibition and synergy effects observed in those two temperature intervals respectively. It is known of course that such phenomena could be the plant membrane protein denaturation [10], [13] at the so-called T_d temperature. Also enzymes such as PME are altered in temperatures of that scale.

As ideas for a future research, more experimentation is required to draw final conclusions on the first findings of the present study. In addition to the *Mentha viridis*, other leafy materials should be examined [14].

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