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Instant Controlled Pressure-Drop DIC to Intensify Drying Kinetics and Rheological Attributes of Carob Seeds

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Abstract: In the food industry, some additives such as carob bean gum are highly sought after thanks to their power to present, even at low concentrations, a particular texture, guaranteeing stability, attending sanitary quality, and improving the taste and appearance of food. The main problem in the valorization of such seeds is the presence of shrinkage phenomenon issued from the airflow drying, which would lead to altering the functional quality. It would be also possible to meet among the problems, the risks of contamination by microbes, insects and larvae. It is obvious that an adequate intensification of the drying should address such issues while preserving the functional quality. The current work aimed at identifying the ability of DIC (instant controlled pressure-drop) processing to confer the seeds higher porosity, better tortuosity, greater exchange surface, that they get better aptitude to dry, to allow an effective decontamination that it can even reach a sterilization level of these seeds, while, by instant cooling, to preserve even improve their own functional (rheological) quality. The kinetic of DIC-assisted airflow drying was analyzed using the phenomenological Coupled Washing/Diffusion (CWD) model. Since DIC is a perfectly controlled high-temperature/short-time process, an adequate Design of Experiment DoE was used through operating parameters of saturated steam pressure (P), processing time (t), and number of cycles (c), to measure the washing starting accessibility and the effective diffusivity. It, also, was possible to assess the functional properties and rheological attributes, for systematically performing the statistical calculation of the DoE using Statgraphics software.

Keywords: Instant Controlled Pressure-Drop DIC; Locust bean gum, Carob germ; Starting Accessibility; Effective Diffusivity; Drying; Coupled Washing Diffusion CWD phenomenological model, Rheological behaviors.

INTRODUCTION

The carob tree is called Ceratonia siliqua L. It belongs to the legume family (Fabaceae), with several derivatives such as Kharroub in Arabic, algarrobo in Spanish, carroubo in Italian, carroubier in French, etc. It is a dioecious tree and its importance keeps high although it is not growing fast enough in the Mediterranean region [1], mainly in Lebanon, Syria, and Palestine. It is distributed in Tunisia, Morocco, as spontaneous or artificial settlements, also widespread in Southern Europe (Spain, Italy), North Africa (Morocco) and Greece. It persists in countries with hot and semi-arid climates such as Australia, America [2, 3]. Indeed, it is an agro-sylvo-pastoral leguminous species, which faces multiple climatic, demographic and economic changes, usually having enormous socio-economic and ecological interests [4, 5]. The carob tree has an ability to develop physiological, morphological and also biochemical adaptation strategies to different degrees of water constraints. Therefore, the carob tree plays an important role in protecting soils from degradation and erosion by deforestation and combating desertification [6, 7], acts against the spread of fires [8]. All components of the carob tree (foliage, flower, fruit, wood, bark, root) are useful and valuable, and the demand for carob products is increasing, contributing to increased carob planting in Mediterranean regions [9].

Abbreviation list

DIC:	Instant controlled pressure-drop
LBG:	Locust Bean Gum
CWD:	Coupled Washing/Diffusion phenomenological model
P:	Saturated steam pressure MPa
t:	Processing time (s)
c:	Number of cycles
Y:	Response
β_i, β_{ii}, and β_{ij}:	the regression coefficients
x_i:	the independent variables
ε_0:	random error
ε_{rel}:	the relative expansion ratio
i and j:	the factor indices.
γ:	Shear strength (s^{-1}),
D_{eff}:	effective diffusivity ($10^{-10}m^2/s$)
W_s:	starting accessibility (g H_2O/100 g db)
χ^2:	Khi squared fit test
R:	Correlation coefficient
τ_0 (Pa):	Flow threshold
η_P (Pa.s):	plastic viscosity

Carob seeds are well appreciated and sought after for their functional qualities and multiple industrial uses [10]. They are oval in shape, small and flattened, with a truncated and crushed basal pole in apical zone, very hard and have great resistance. They consist of three parts: the integument, the endosperm, and the germ. Its seed coat is smooth, representing 30 to 35% of the dry weight of the reddish-brown, glossy seed [11], which covers the seed and consists mainly of cellulose, lignin and tannin. The second part is the endosperm which represents 40 to 50% of the weight of the seed [12]. It is the most interesting part since it constitutes the reserve tissue coating a germ or embryo, has a high content of galactomannan or carob gum, which is crude [13]. The third part is the germ, representing 15 to 30% of the dry weight of the seed [12], used as a substitute for a diet as well as for livestock nutrition [14]. It is soluble in water and unsaturated lipids has a high energy value due to its high protein content [15]. In addition, the germ or rootlet contains a number of enzymes; such as endo-1,4-ß-mannanases, α-galactosidases and ß-mannosidases, capable of hydrolyzing galactomannans during germination [16].

“Carob bean gum” or more commonly "locust bean gum" (LBG) known as E410 in food additives [17], is marketed as a whitish powder [18]. Galactomannans have a structure mainly consisting of a chain of mannan on which there are branches of a galactose unit linked in α (1-6) [19]. In addition, the chemical composition of commercial carob bean gum includes 1% cellulose and lignin, 1% lipids and 1% minerals, 4% proteins, and 10 to 13% moisture, and the largest amount is galactomannan from 80 to 85% [20, 21]. After purification, carob bean gum removes cellulose and lignin and lipids and reduces the amount of minerals [22]. Their function is to serve the food reserve to the embryo during germination, the purification stage consists of solubilizing flour and precipitating galactomannans to eliminate impurities [15]**.** Food gums are polysaccharide substances capable of thickening, gelling and stabilizing a solution, even at low concentrations. In view of these physicochemical functional properties, gums are used as a raw material in the food industry, to thicken solutions for sauces, drinks and mayonnaises; Stabilize suspensions and emulsions for sauces, chocolate milks; Fix water and delay the crystallization of charcuterie products, and ice creams and form gels during the formation of jams and gelled desserts [23]. Moreover, the interest of polysaccharides is not limited to their rheological properties which have a biological role of some of them as molecules with pharmaceutical activities by tablet encapsulations [24, 25] and cosmetics [26, 27] and more recently in the oil industry and also as an anti-diarrheal product [28]**.** They are mainly water-soluble polymers causing an increase in the viscosity of the aqueous medium. The locust been gum have the property of swelling in cold solutions.

Knowing that in many extraction operations carried out on plants, the natural structure is so compact that it implies a very low coefficient of diffusion of the liquid within the solid matrix, the present research work aims to study the effect of controlled instantaneous pressure drop (DIC) texturing on carob seed, in terms of analysis of the impact of texturing on the different parts of the seed (locust bean gum and germ) which involve a modification of the structure. DIC texturing consists of heating under high pressure with saturated steam (0.2-0.7 MPa or 110-160 °C) for a short period of time (a few tens of seconds) [29-31], followed by an instantaneous pressure drop (20-40 ms) towards vacuum (3-5 kPa) [32]. The very abrupt evolution of the system implies an autovaporization of a quantity of water, generating mechanical stresses within the solid matrix and implying the possibility of resulting in an expanded structure of the material [33]. The process is intimately coupled with such rapid cooling generally exceeding the equilibrium state (thermodynamics of instantaneity) and inducing preservation of the new structure by asymptotically approaching the glass transition Tg. The specific intensification obtained by the DIC treatment also implied a great preservation of the quality of the finished product [34], while indicating an improvement in airflow drying kinetics [35, 36] of locust bean gum and germ of carob treated with DIC compared to those not treated. In addition, the impact of these operations on functional behavior will be analyzed in terms of the rheological impacts of carob bean gum.

MATERIALS AND METHODS

Sampling of Carob Seeds

The carob seeds were randomly chosen from several trees representative of the Lebanese population, in a geographical area not exceeding 500 m^2 in Mount Lebanon Shhim and Northern Lebanon in Batroun and Selaata. The samples were packed and stored in a cold room at 4°C. The initial water content (Wi) of locust bean is approximately 0.16 ± 0.005 g water/g db.

Experimental protocol of extraction of carob seeds

In this experimental laboratory study, carob seeds were subjected to various treatments aiming at the separation of the different components: cuticles, endosperm or gum and carob germ. The experimental protocol of DIC texturing of carob seeds was carried out by a simple preparation (Figure-1). As a pre-treatment, 500 g carob seeds were put in a beaker and stored for 24 h in a refrigerator that they reached a rehydration until an intermediate water content (Wi) of approximately 0.35 ± 0.005 g H_2O/g db. Then, the seeds were pulled and put into a Moulinex machine where they are subjected to a centrifugal force and a contact force. Then, a seed washing step will be carried out under a jet of tap water, then rubbed by hand through a 2-mm metal strainer.

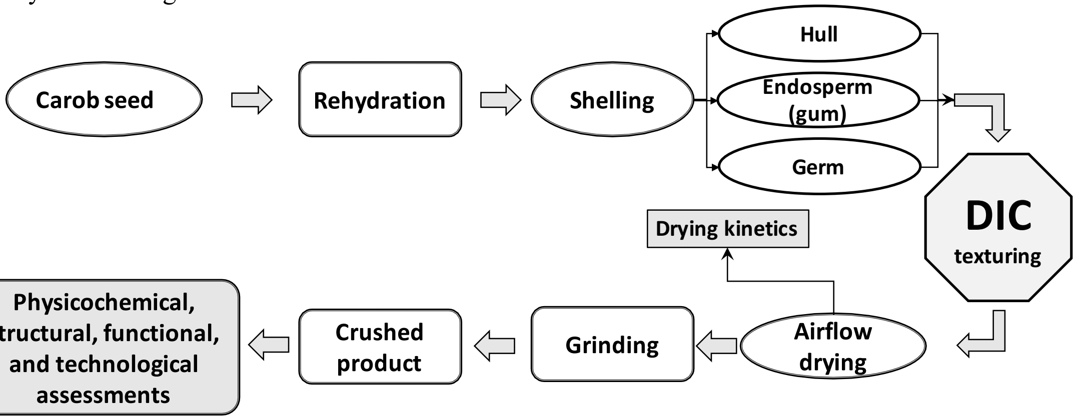

Fig-1: Carob Seed Application Protocol

The seed cuticle becomes fragile and easy to separate from the endosperm. They swell, it is the phenomenon which results from the diffusion of water, leads to the manual separation of the endosperm from the germs. In the second part of our experimental study and after separating the different parts of grains, the locust bean gum and germ of carob were subjected to a thermo-mechanical treatment by instant controlled pressure-drop (DIC) with the aim of intensifying the raw material through a controlled modification of the structure which implies a preservation of the quality of the finished product, while indicating an improvement in the drying kinetics of the air flow. In addition, we studied the impact of texturing on the rheological behavior of carob bean gum.

Rehydration kinetics

It was necessary to insert a rehydration step as pre-treatment before achieving the DIC texturing. The rehydration kinetics were studied at room temperature (20°C) as a function of time $\alpha = f(t)$. Values of rehydration water content dry basis were evaluated at different soaking time of 5, 120, 180, 240, 300, 480, 900, and 1440 min. The rehydration kinetics depends on several product characteristics (nature, biochemical composition, physical properties, surface specificity, size, porosity and density and manufacturing processes, etc.) but also on the rehydration conditions (temperature, agitation speed, solid/liquid concentration, etc.).

Treatment process of Instant controlled pressure drop DIC

Description of the DIC equipment

The DIC [37] unit involves three main elements (Figure-2).

- A cylindrical treatment vessel of 13 liters in which the products are treated.
- A vacuum system consisting mainly of a water-ring vacuum pump of an absolute pressure close to 4 kPa in a large tank of 1.6 m^3, namely 130 times greater than the treatment vessel.
- A large-section (about 20 cm in diameter) instantaneously opening pneumatic valve; it offers an abrupt connection (less than 50 ms) between the treatment vessel and the vacuum tank.

Treatment process

- The DIC treatment is based on hydro-thermomechanical effects mainly based on an instant pressure-drop following a stage of heating at high absolute pressure. Temperature and pressure correlations during a DIC cycle were illustrated in Figure-3. A DIC treatment can be acting as a multi-cycle with several repetitions of the steps and each cycle, which is composed of five steps:

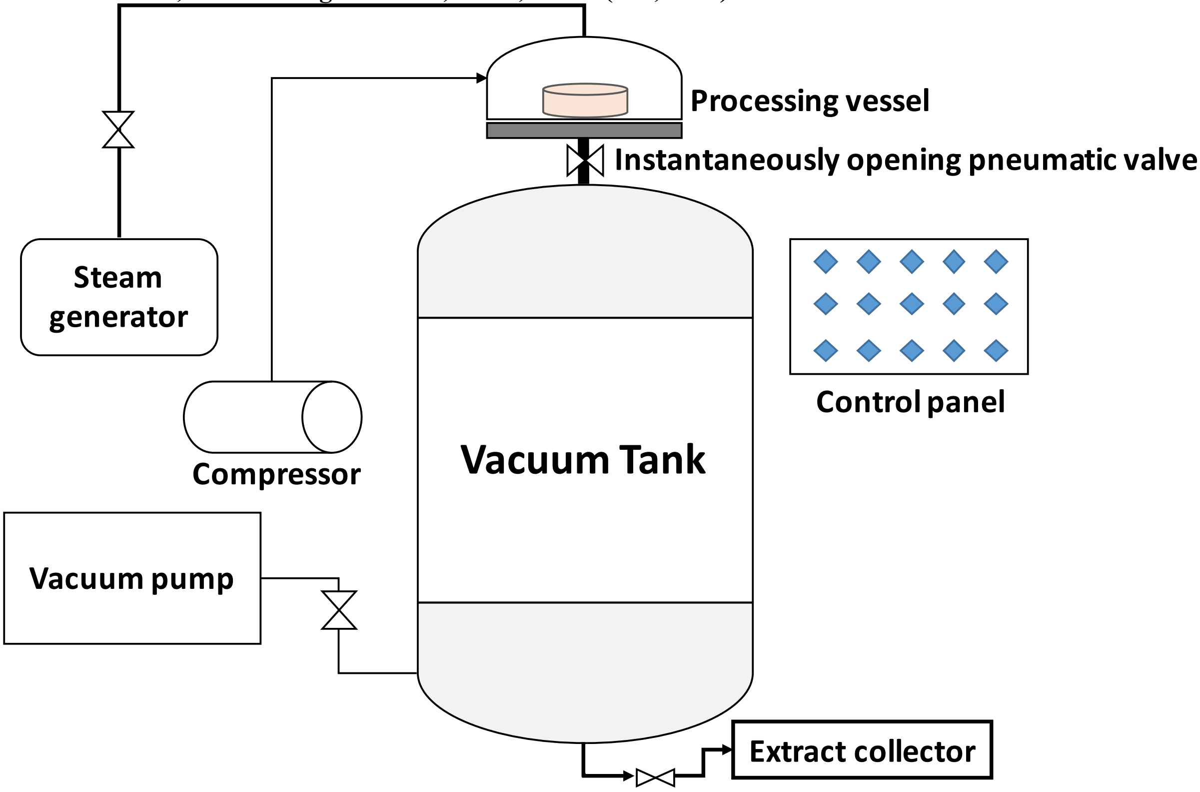

Fig-2: Schematic diagram of the DIC reactor

At first, the samples of the locust bean gum and the germ of carob were placed in the vacuum processing chamber, then they were submitted for a short period of about 5 to 15 seconds to an injection of saturated steam at high pressure and kept constant for a predetermined time, here between 0.2 and 0.5 MPa. After this heating step [38], the pneumatic valve, opened in less than 50 ms, to connect the treatment chamber to the vacuum tank, such inducing an abrupt (instantaneous) pressure drop towards the vacuum of about 5 kPa, causing a partial autovaporization of a part of the water contained in the product and an instant cooling of the products [39]. This immediately stops the thermal degradation while possibly producing an expansion more or less marked on the locust bean gum and germ of carob [32]. The last-step is characterized by a releasing of the pressure towards the atmospheric level. DIC treatment is a texturing operation whose main objective is to obtain a modification of the carob structure in order to control the impact of intensification on the different parts of the seed and to improve (or preserve) the total functional quality of the powder.

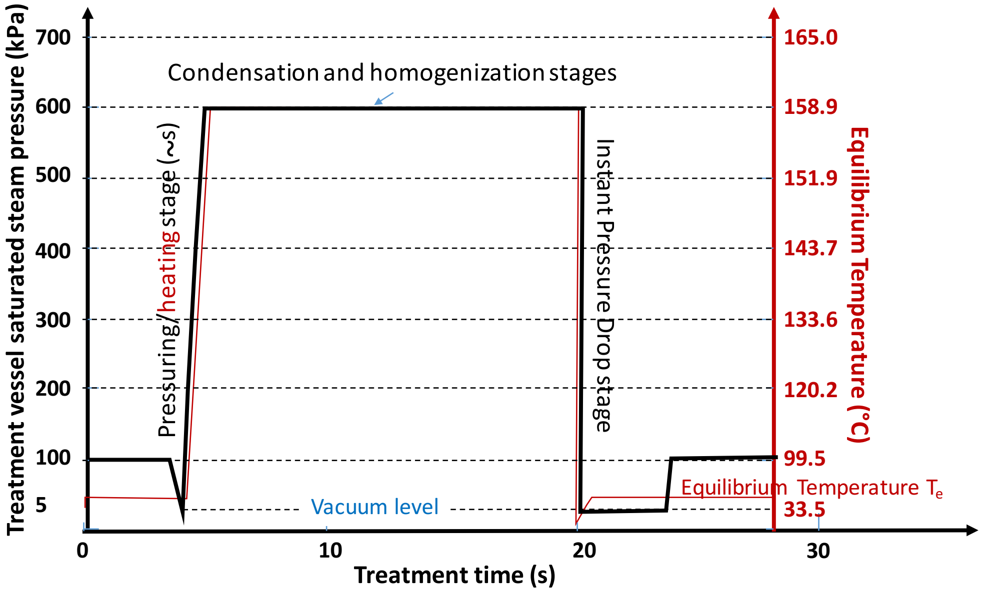

Fig-3: Correlated temperature and pressure variation during a DIC treatment

Our experimental work consisted of applying a treatment to extract the locust bean gum powder and the germ, which were then analyzed and characterized in terms of physicochemical composition, and structural, functional and technological properties versus the operating conditions. Following preliminary tests and basing on previous work, we selected the three DIC processing parameters of saturated dry steam pressure (P), treatment time (t), and number of cycles (c) to identify their impacts on the different components of the carob seed (gum and germ).

Drying process and study of kinetic

Following the DIC treatment, convection drying was performed in a ventilated oven type MEMMERT GmbH & KG (model 800, SCHWABACH GERMANY) with 40°C; 3 m/s, and RH of 14%. The drying kinetics was identified vs the time W=f(t), by weighting the samples at regular time intervals.

Kinetic analysis and fundamental modeling

The fundamental analysis of drying kinetics was based on a phenomenological Coupled Washing/Diffusion CWD model. By assuming Negligible External Resistance NER conditions of drying, this can be presented as including a diffusion stage following a washing stage. The parameters of starting accessibility δW_s and effective diffusivity D_{eff} were identified and used as responses able to reveal the impact of DIC intensification on airflow drying.

The effective diffusivity D_{eff} was expressed in 10^{-10} m^2/s defining the long-term process occurring between the interior part of the matrix and the surface. Following a DIC treatment, this parameter increases with the porosity, tortuosity, and the expansion ratio. Usually, such an increase can reach up to 10 times more of the raw material. This parameter was calculated after assuming that the external transfer resistance was negligible compared to the internal heat and mass transfers. Thus, D_{eff} was calculated through the concentration gradient based on the first FICK law within porous materials. Mounir and Allaf [33] considered that when there is no significant shrinkage of the product after the DIC treatment and by assuming the homogeneity of product structure and temperature, the Crank standard solutions can be proposed to reveal the main required solutions.

$\mathrm{Ln}(Y) = Ln\left(\frac{(w_{\mathrm{d}\infty} - w_{d0})}{(w_{\mathrm{d}\infty} - w_{\mathrm{d}})}\right) = \mathrm{kt} + \mathrm{constante}$	*Eq. 1*

The effective diffusivity D_{eff} of a spherical material with d_p as diameter or infinite plate material with e_p as half thickness is calculated following a relationship between the experimental data and the diffusion model using the Crank polynomial expression:

Hypothesis of spherical material:	$D_{eff} = \frac{d_p^2}{\pi^2}k$	*Eq. 2*
Hypothesis of infinite plate material:	$D_{eff} = \frac{4e_p^2}{\pi^2}k$	*Eq. 3*

Since the washing step is revealed by the initial accessibility δW_s expressed in g H_2O/100g db (dry basis) consisting of a short-time surface interaction between the airflow and the surface (convection heat and vapor transfers), this is a free-of-diffusion step. The starting accessibility δW_s is obtaining by extrapolating the diffusion model to t=0 min getting a theoretical value W_0, and then, by calculating the difference between the initial real experimental value W_i and the calculated theoretical value W_0:

$\delta W_s = \mathrm{W_i} - \mathrm{W_0}$	*Eq. 4*

Seed grinding

After DIC texturing, dried products such as locust bean gum and germ of carob were ground using the laboratory knife mill Grindomix, GM200-F. (Kurt Retsch GmbH & Co. KG, Haan, Germany) at a speed of 10,000 rpm/min for 60 seconds. They were prepared for different analyses.

Experimental strategy

Design of Experiment DoE

Preliminary experiments of DIC texturing of the carob seeds allowed identifying the variation ranges of the different operating parameters in terms of significantly intensifying the airflow drying of locust bean gum and germ of carob. A five-level rotary central composite Design CCD of Experiment DoE relevantly coupled with the response surface methodology (RSM) was defined picking up the three independent parameters of DIC; 1/ the absolute pressure P of the saturated dry steam ranged from 0.2 to 0.7 MPa, 2/ the processing time t between 30 and 60 s, and 3/ the number of cycles c ranged from 1 to 7 (Table-1). This 22-trial DoE was implemented with 8 central points labelled as (ACP).

Table-1: The processing parameters and ranges of saturated steam pressure P, processing time t and number of cycles in the DIC-texturing of locust bean gum and germ of carob

	Coded level				
	(-α)	(-1)	(0)	(+1)	(+α)
P: Saturated dry steam pressure (MPa)	0.2	0.30	0.45	0.60	0.7
t: Total processing time (s)	30	36	45	54	60
C: Nb of cycles	1	2	4	6	7

Statistical analysis

The main responses to the results were statistically analyzed using the Statgraphics Plus for Windows analysis design procedure (Statgraphics Centurion XV, StatPoint Technologies, Inc., Rockville, USA). This RSM highlights for each Y-dependent variable response parameter the level of significance of the DIC factors as an independent variable x_i across the ANOVA levels with a p-value =0.05. The Pareto diagram includes the standardized impact of various independent factors (linear impacts x_i, square impacts x^2_i, and interaction impacts x_ix_i) positioned relative to a vertical bar indicating the significant impact level. The general trends, the response surfaces, as well as the second order empirical model with the regression coefficient R^2 and the optimal values help to identifying the impact of each DIC factor.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i \chi_i + \sum_{i=1}^{k} \beta_{ii} \chi_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} \chi_i \chi_j + \varepsilon_o \qquad \textit{Eq. 5}$$

Assessments of characteristics

Measure of moisture content

The water contents W expressed in g H_2O/g db (dry basis) and H (% wet basis) were assessed according to the AOAC method 2005. A sample quantity of 2 to 3 g ± 0.5 g of sunflower powder was precisely weighed and placed in aluminum cups (three replicates). This was then placed open in an oven (Memmert, Germany) at 105 °C for 24 hours. When it came out of the oven, the cups were cooled in a desiccator for a period of time to prevent any moisture regain and then weighed. It was also measured with an Infrared Balance (Mettler Toledo LP-16 Infrared Dryer/Moisture Analyzer with Mettler Toledo PE360 Balance - Bishop International Akron, OH - USA) set at 105°C. It is worth noting that water contents dry basis W and wet basis H are correlated as:

$$\mathrm{W\ (g\ H_2O/g\ db)} = \frac{\mathrm{H}}{1-\mathrm{H}} \qquad \textit{Eq. 6}$$

Measurements of Rheological Properties of locust bean Gum

Measurements of rheological properties and flow behavior of locust bean gum were performed using a VT550 HAAKE rheoviscometer (Germany). The cone used was pk5/0.5°. The program for the analysis of the evolution profile of a flow test was carried out according to pre-determined conditions with a plateau temperature of 23 °C. For flow measurements, the swept shear rate ramp was ranged from 0 to 10^3 s^{-1} for a test duration of 180 s. This allowed obtaining the flow curve ($\tau = f(\gamma)$) corresponding to the best rheological model (adjusted with the lowest adjustment χ^2 and highest correlation coefficient "R" > 0.7. The solution was prepared by weighing 0.6 g of carob powder to be dispersed in 10 ml of distilled water, ie a concentration of 6%. The mixture is homogenized for one minute at room temperature (30 ± 0.2 °C). 5 g of prepared gel are placed on the rheoviscosimeter plate.

RESULTS AND DISCUSSIONS

Analyses of airflow drying

Kinetic of drying of carob seeds

Table-2 brings together all the experimental and modeled data of the kinetics of airflow drying in the case of locust bean gum.

Kinetic model parameters (Starting accessibility, Effective diffusivity) of locust bean gum and carob germ

Fig-4 of the water content dry basis versus time highlights a specific intensification of airflow drying obtained with DIC-textured samples relative to the raw-material RM. The DIC-assisted airflow drying improved kinetics while preserving quality. Therefore, the untreated samples spent about 870 min to allow water content W to evolve from 0.5 to 0.1 g H_2O/g db, against 120 min for DIC-treated sample under a saturated dry steam pressure P= 0.3 MPa, for total processing time t=54 s, and a number of cycles c = 6.

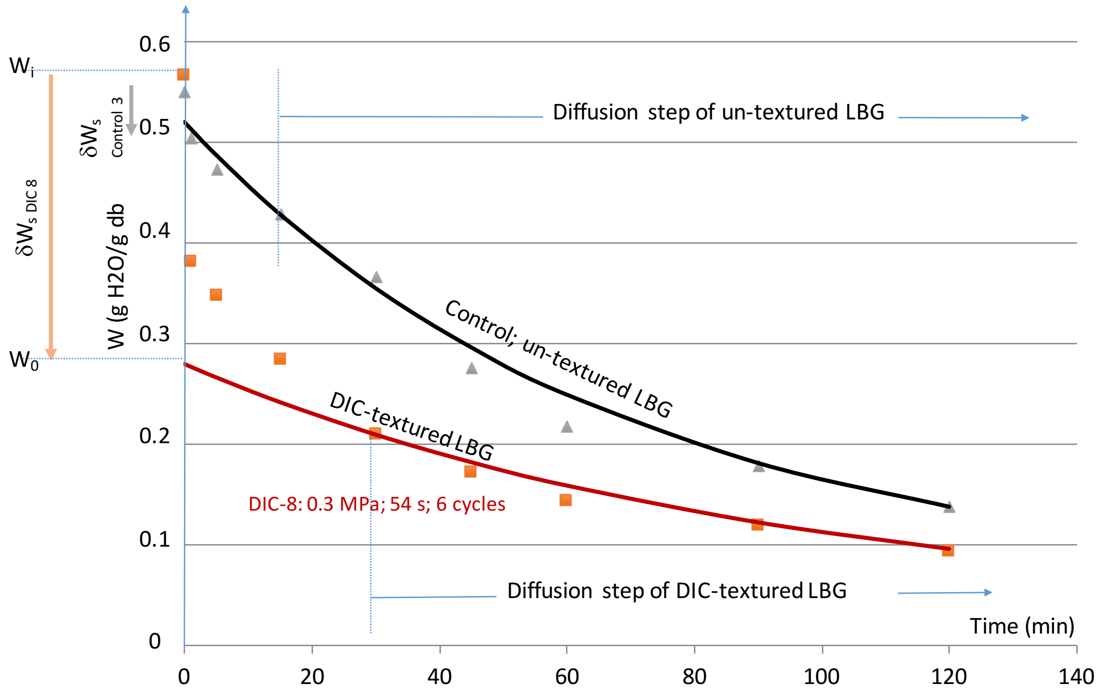

Fig-4: Drying kinetics of DIC-8 treated (54s; 300 kPa; c=6 cycles) and un-textured locust bean gum LBG

The experimental results of airflow drying kinetics of the various DoE trials were analyzed using the phenomenological Coupled Washing/Diffusion (CWD) model, issued from assuming Neglected External Resistance NER airflow parameters. The impact of DIC while texturing locust bean gum LBG and carob germ was established through the starting accessibility δW_s (g H_2O/g db) and the effective diffusivity D_{eff} ($m^2\ s^{-1}$) of the water within the porous solid, coupled with the relative expansion ratio ε_{rel} (%).

Table-2: The main response of DIC's intensification of airflow drying of locust bean gum LBG: thickness e (mm); the relative expansion ratio ε_{rel};; the water effective diffusivity within the material D_{eff} (10^{-10} m²/s); and the starting accessibility δW_s (g H_2O/g db).

run no	t (s)	P (MPa)	c	e	ε_{rel}(%)	D_{eff}	RI_{Deff} (%)	δW_s	$RI_{\delta Ws}$ (%)
RM	-	-	-	1.122	98.000	0.13	100%	0.026	100%
1	45.00	0.45	4	1.432	125.000	1.26	969%	0.079	304%
2	60.00	0.45	4	1.342	117.000	0.313	241%	0.114	438%
3	45.00	0.45	7	1.216	106.000	0.691	532%	0.083	319%
4	45.00	0.45	4	1.444	126.000	0.3	231%	0.106	408%
5	45.00	0.70	4	1.272	111.000	1.931	1485%	-0.023	-88%
6	45.00	0.20	4	1.400	122.000	0.324	249%	0.107	412%
7	45.00	0.45	4	1.248	109.000	0.161	124%	0.116	446%
8	53.92	0.30	6	1.200	105.000	0.139	107%	0.113	435%
9	36.08	0.30	2	1.364	119.000	0.343	264%	0.083	319%
10	45.00	0.45	4	1.354	118.000	1.117	859%	0.05	192%
11	53.92	0.30	2	1.386	121.000	0.337	259%	0.083	319%
12	36.08	0.60	6	1.100	96.000	0.775	596%	0.047	181%
13	45.00	0.45	4	1.230	107.000	0.308	237%	0.058	223%
14	36.08	0.60	2	1.240	108.000	0.236	182%	0.111	427%
15	36.08	0.30	6	1.318	115.000	0.161	124%	0.073	281%
16	45.00	0.45	4	1.342	117.000	0.195	150%	0.08	308%
17	30.00	0.45	4	1.272	111.000	0.255	196%	0.049	188%
18	53.92	0.60	6	1.220	106.000	0.939	722%	-0.008	-31%
19	45.00	0.45	4	1.266	110.000	0.197	152%	0.053	204%
20	53.92	0.30	2	1.420	124.000	0.363	279%	0.043	165%
21	45.00	0.45	1	1.386	121.000	0.94	723%	0.014	54%
22	45.00	0.45	4	1.304	114.000	0.326	251%	0.037	142%

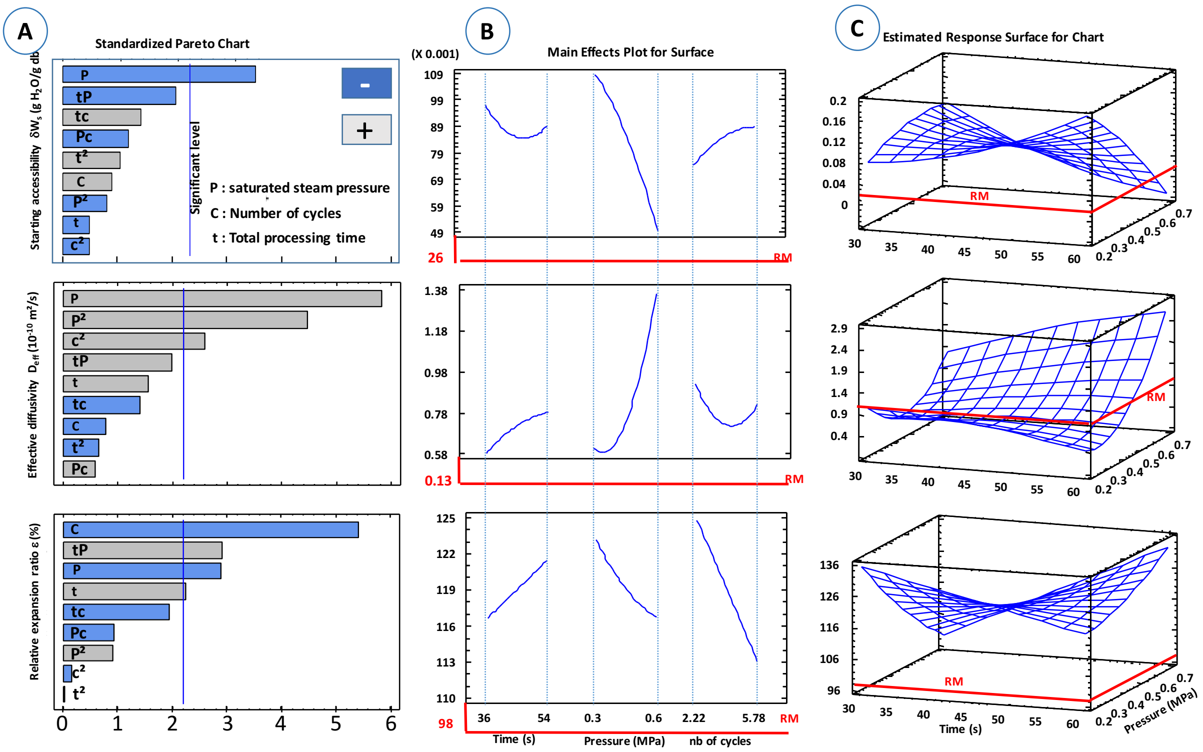

Fig-1: Effect of DIC parameters on locust bean gum: A) Pareto Chart; B) Main Effects Plot; C) Estimated Response Surface.

Indeed, once NER airflow drying conditions were assumed, the effects of DIC operating parameters on the kinetic parameters were identified from through CWD phenomenological model. They significantly elucidated positive effects of the DIC treatment on the water diffusivity within the material D_{eff} (10^{-10} m²/s) and the starting accessibility δW_s (g H_2O/g db). They increased from 0.13 to 1.93 10^{-10} m²/s and from 0.026 to 0.116 g H_2O/g db, respectively. The relative expansion ratio was about ε_{rel}=126% compared to the untreated carob gums.

The statistical study using Statigraphic software allowed classifying the kinetic and functional parameters through graphic presentations of the standardized Pareto diagram (Fig-5.A), the main trend diagram, and the response area (Fig-5 B and C). The most significant independent processing parameters of P, t and c for each response of the the starting accessibility δW_s, the effective diffusivity of water within the material D_{eff}, and the relative expansion ratio ε_{rel}, as dependent parameters were identified.

Table-3 presents the empirical models of second order of locust bean gum allowed to identify the optimized operating parameters, which were (60 s; 0.2 MPa; 7 cycles) with 0.28 g H_2O/g db for the starting accessibility, (60s; 0.7MPa; 2 cycles) for 3.11 10^{-10} m²/s for the effective diffusivity and 149.5% for the expansion ratio, with an appropriate adjustment to the experiments revealed by the regression coefficients of R^2= 69.46 %, R^2= 88.35%, and R^2=88%, respectively. Effective drying process intensification of locust bean gum of carob was obtained by DIC treatment.

Table 1. Empirical models retained from the second-order regression of locust bean gum of carob: *Starting accessibility δW_s (gH₂O/g db)*; Effective Diffusivity D_{eff} (10^{-10}m²/s) and Relative *expansion ε_{rel} (%)*.

δW_s (gH_2O/g db) $=0.04-0.0056t+1.054p-0.0098c+0.0001t^2-0.018tp+0.00102tc-0.27p^2-0.0516pc-0.00115c^2$ (R^2=69.46%)
D_{eff} (10^{-10}m²/s) $=2.985+0.0260t-14.721p-0.147c-0.00048t^2+0.13tp-0.0077tc+11.74p^2+0.19pc+0.047c^2$ (R^2=88.35%)
ε_{rel} (%) $=161.685-0.497t-184.662p+7.664c+0.00026t^2+3.287tp-0.183tc+40.533p^2-5.234pc-0.0485c^2$ (R^2=88.00%)

Similar behavior was observed with DIC-textured carob germ against non-treated germ (RM). This confirms that DIC treatment implies an improvement in the airflow drying operation and ensures that the quality of the product is preserved. Table-4 shows the treatment with DIC significantly improved the effective diffusivity of the germ samples to be 2.5 10^{-12} against 0.36 10^{-12} m^2 s^{-1} for the raw material (RM).

Similarly, the starting accessibility for DIC-treated germ reached 0.63 against 0.08 g H_2O/g db for non-treated germs. This would be related with the expansion of the germ brought by DIC, which implied a relative expansion ratio ε_{rel} up to 236%. The statistical processing of the results led to the identification of the Pareto diagram, general trends, and response surfaces versus the operating parameters (P, t, and c) in terms of starting accessibility and effective diffusivity (Figure-6 A, B, and C).

Table-2. The main response of the intensification of the drying of the carob germ in terms of the thickness e (mm), the relative expansion ratio ε_{rel} (%), and the effective diffusivity D_{eff} (10^{-10} m^2/s), and the starting accessibility (g H_2O/g db) each versus DIC's factors: Pressure P, treatment time t, and number of cycles C.

run no	P (MPa)	t (s)	C	e (mm)	ε (%)	D_{eff}	RI_{Deff} (%)	δW_s	$RI_{\delta Ws}$ (%)
RM	-	-	-	0.933	100	0.36	100%	0.087	100%
1	45.00	0.45	4.00	0.983	108	0.451	125%	0.432	497%
2	60.00	0.45	4.00	1.137	124	1.446	402%	0.466	536%
3	45.00	0.45	7.00	1.137	124	0.365	101%	0.424	487%
4	45.00	0.45	4.00	1.117	122	0.549	153%	0.358	411%
5	45.00	0.70	4.00	1.097	120	1.435	399%	0.304	349%
6	45.00	0.20	4.00	1.067	117	0.956	266%	0.336	386%
7	45.00	0.45	4.00	1.400	153	0.868	241%	0.333	383%
8	53.92	0.30	5.78	1.057	116	0.985	274%	0.418	480%
9	36.08	0.30	2.22	1.047	115	0.566	157%	0.447	514%
10	45.00	0.45	4.00	1.147	126	0.484	134%	0.371	426%
11	53.92	0.30	2.22	1.120	123	0.381	106%	0.417	479%
12	36.08	0.60	5.78	1.070	117	1.233	343%	0.382	439%
13	45.00	0.45	4.00	1.087	119	0.394	109%	0.307	353%
14	36.08	0.60	2.22	2.153	236	2.216	616%	0.482	554%
15	36.08	0.30	5.78	0.887	97	0.644	179%	0.332	382%
16	45.00	0.45	4.00	1.157	127	1.25	347%	0.434	499%
17	30.00	0.45	4.00	1.053	115	0.923	256%	0.422	485%
18	53.92	0.60	5.78	1.240	136	1.57	436%	0.414	476%
19	45.00	0.45	4.00	1.067	117	1.096	304%	0.427	491%
20	53.92	0.30	2.22	1.263	138	1.294	359%	0.5	575%
21	45.00	0.45	1.00	1.247	136	1.45	403%	0.471	541%
22	45.00	0.45	4.00	1.443	158	2.553	709%	0.631	725%

The empirical second-order regression models of Table-5 were obtained for the effective diffusivity and starting accessibility of locust bean germ airflow drying. They got almost relevant regression coefficients of R^2 (81.5 and 68.5%, respectively). It was possible to determine from these models the optimal operating parameters of DIC-texturing for getting the highest values of D_{eff} and δW_s. They were 4.01 10^{-10} m^2/s and 0.75g H_2O/g db., respectively, for the operating conditions of (t=38 s, P=0.2 MPa, and 1 cycle) and (t=30 s, P=0.2 MPa, and 1 cycle), respectively.

Table-3. Empirical models retained from the second-order regression of germ of carob

δW_s (gH_2O/g db)=1.150-0.0260t+1.320p-0.172c+0.00031t^2-0.017tp+0.0016tc-0.875p^2+0.048pc+0.0081c^2	R^2=81.58%
D_{eff} ($10^{-10}$$m^2$/s)=7.060-0.236t-1.377p-0.368c+0.0027t^2-0.0493tp+0.0066tc+9.8960p^2-0.745pc+0.0364c^2	R^2=68.52%

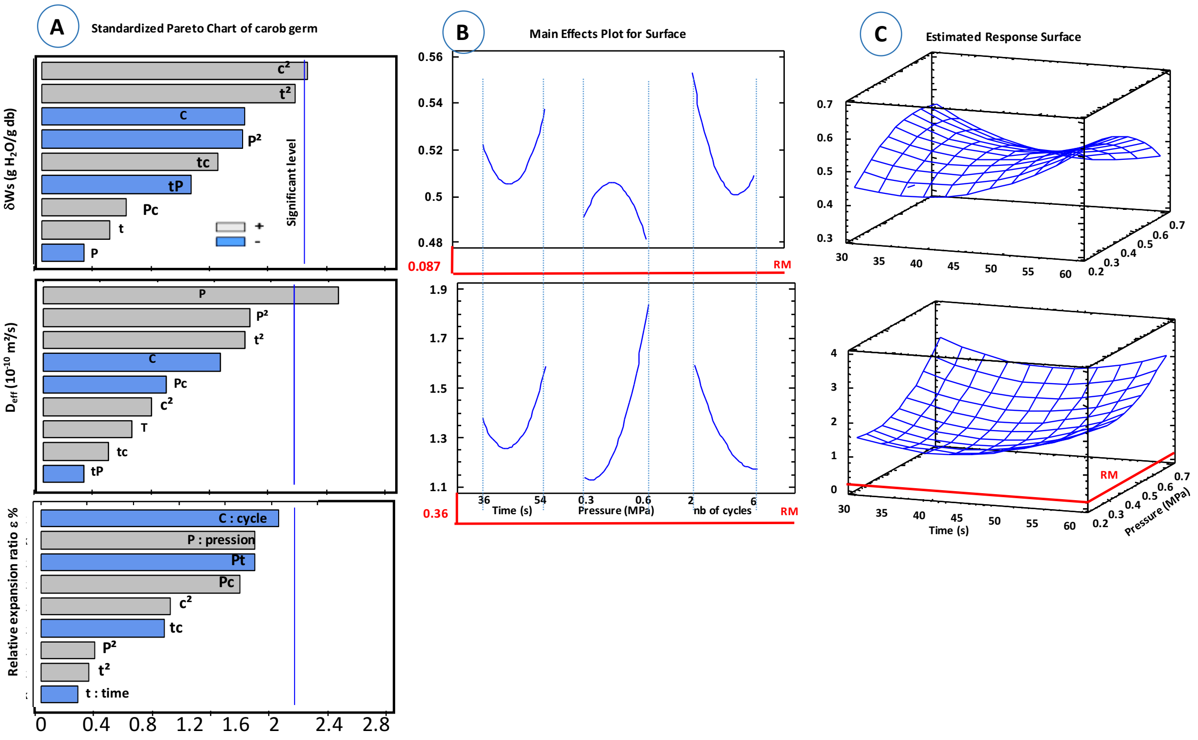

Fig-2: Effect of DIC parameters on carob germ: A) Standardized Pareto Chart; B) Main Effects Plot; C) Estimated Response Surface. Since the processing parameters were with non-significant effects, their own trends and response surface were not presented.

Effect of DIC parameters on Rheology of locust bean gum

Table-6 describes an adequate DoE experimental design used through the operating parameters of saturated vapor pressure (P), processing time (t) and number of cycles (c). The responses as dependent parameters were different rheological characteristics such as flow threshold τ_0 (Pa) and plastic viscosity η_P (Pa.s).

The rheometer analyses showed that the samples treated by DIC presented a Casson type plastic behavior, with significantly the lowest chi-square and the highest correlation coefficients attesting to the good fit of the model. The equation of Casson's model is as follows:

$$\tau^{0.5} = \tau_0^{0.5} + \eta_P \gamma^{0.5}$$

Eq. 7

More than only preserving a major part of functional rheological characteristics of carob bean gum, DIC texturing was able to improve the viscosity profiles and the flow behavior, with a specific impact of temperature. The properties of the DIC-treated samples were compared with those of the non-treated of locust bean gum of carob.

Table-6: Adjustment parameters of Casson's rheological model with the main responses of carob bean gum (R^2=0.96-0.99)

N° of trial	RM	APC	2	3	5	6	8	9	11	12	14	15	17	18	20	21
χ^2	7.53	27± 16	20	21	35	47	12	5	37	22	25	22	27	23	33	15
τ_0 (Pa)	0.97	21± 13	19	10	33	40	13	5	26	12	15	14	20	19	21	10
η_P (10^{-2} Pa.s)	6	11± 4	8	2	9	8	10	12	11	10	07	8	10	7	9	11

Furthermore, the effects of the DIC parameters were revealed through the second order empirical models (Table-7) of the flow threshold and the viscosity expressed as functions of the operating parameters (P, t, and c). The optimal value of viscosity was close to 0.46 Pa.s at the conditions of (45s; 4 MPa; 4 cycles); and a flow threshold of 35 Pa for (48 s; 7 MPa; and 4 cycles) with satisfying adjustment values R^2 = 70,5%; 74,87 %; and 74,89 %, respectively.

The statistical analysis of rheological data issued from DIC-textured and untextured raw material allowed highlighting that DIC treatment systematically increase the values of τ_0, and η_P (Figure-7, A, B, and C).

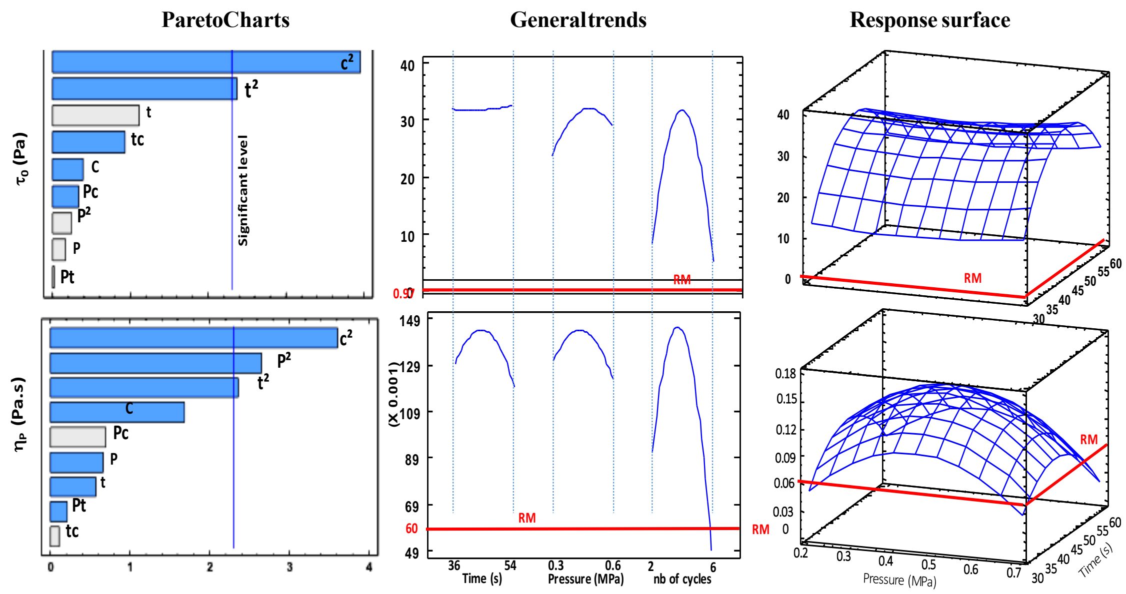

Figure 3. Effect of DIC parameters on rheology of locust bean gum.

Table-7. Empirical models retained from the second-order regression of rheology of locust bean gum

τ_0 (Pa)=$-63.17+2.94t-152.09P+23.21c-0.022t^2+0.14tP-0.189tc+185.34P^2-4.413Pc-1.65c^2$	R^2=74,72%
η_P (10^{-3} Pa.s)=$-500+71P+19t+43c-9P^2-0.2Pt+2.7pc-0.2t^2+0.07tc-8c^2$	R^2=74.29%

Industrial application

An industrial unit of DIC treatment coupled with an airflow drying of carob seeds was predicted for an hourly capacity of 1200 kg/h. The optimized DIC conditions were adopted; they were 0.3 MPa, for 45 s. DIC-assisted airflow drying has required 2 h instead of about 15 h for the conventional airflow drying, both carried out at 40°C, 3 m/s and 6.5% relative humidity HR. DIC resulted in great reduction of equipment cost and energy consumption. Indeed, the heat energy required for 1 hour of DIC has corresponded to 163 kWh of steam, and 12 kWh of electrical energy including a specific cooling system of vacuum tank.

The rheological quality of final product also implied a higher economic impact. Thus, by incorporating the optimized DIC texturing pre-treatment conditions, the industrial operations of drying, hulling, and separation, crushing, and packaging of both locust bean gum and germ got much higher production capacity with high final product quality.

These findings have been of great potential importance from industrial point of view in term of cost effective carob valorization and production. More interest would be obtained from expanded fruits possibly increasing the rehydration and the production of carob concentrate; this shall be the object of a future research work.

CONCLUSION

The Instant Controlled Pressure Drop "DIC" texturing technology effectively assists the airflow drying of carob seed in both process performance and functional quality. This is a process intensification way able to preserve or even improve the functional rheological behavior of locust bean gum. The effect of the DIC treatment in terms of drying kinetics of both locust bean gum LBG and germ of carob was studied with airflow at 40°C, 3 m/s and 6.5% relative humidity HR. DIC texturing considerably and systematically reduced the drying time. The experimental study was based on defining a central composite design of experiments CCD-DoE, and RSM (the Response Surface Methodology) was performed via statistical analyses done by Statgraphics. Thus, preliminary trials and the know-how of the concerned laboratories allowed selecting the operating factors of saturated dry steam pressure (P), processing time (t) and number of cycles (c) as the independent variables and consider their various impacts on drying kinetics. Numerous similar operations carried out in similar drying conditions have allowed the operation to be considered as Negligible External Resistance NER. Hence, we adopted the phenomenological CWD (coupled Washing/diffusion) model to relevantly define the drying kinetics through the effective diffusivity D_{eff} and the starting accessibility δW_s.

Other part of this study has concerned the assessments of rheological behavior. The DIC treatment had a positive effect since it takes place as a well-controlled texturing process. It appeared as so controlled operation able to modify and even improve the rheological properties which are essential in defining the functional properties of carob germ and locust bean gum.

Furthermore, the mechanical effect of the abrupt pressure-drop provides a highly relevant autovaporization resulting in a well-controlled expanded matrix. Hence, DIC-assisted airflow drying, commonly called swell-drying, allowed the development of a new transformation process specifically for locust bean gum and germ of carob that it can be used at industrial scale to obtain a high and well-controlled quality product. Moreover, it is well-known that the higher the drying kinetics, the lower the required drying energy. Such a DIC expansion systematically causes an improvement in the technological aptitude of the material according to its new structure. Thanks to its nature as High-Temperature/Short-time HTST operation, DIC treatment allowed a better preservation of the rheological properties of Locust bean gum in terms of viscosity profiles and flow behavior as a function of temperature.

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