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Compilation of Rheological Models and Their Application to Tomato Sauce (15°Brix) (Solanum Lycopersicon)

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Abstract

We have compiled rheological models, which are, in our opinion, the most important in the food industry. We affirm that rheological models from elementary to the most complicated possible ones have been found during the search. Under the conditions of concentration (15°Brix) and process temperatures, tomato sauce (Solanum Lycopersicon) rheologically behaves according to the Herschel-Buckley model and the Standard Error of Estimate (SEE) for the consistency coefficient (K_1) and the melt flow index (n) were 0.3556 and 0.0587. The rheological models work according to the wide range of foods and their different difficulties. In addition, the rheological models depend on the types of food, mainly solid, pseudoplastic, and liquid foods. Within each food group, there are other subgroups describing different and more complicated rheological models than the first ones. There are predetermined models defined for each food. However, when the food undergoes a slight variation, it rheologically changes and therefore its rheological model too; this situation is present in tomato sauce (Solanum lycopersicon). Eventually, the purpose of the research has been satisfactorily fulfilled, at the conditions of the study, determining that the rheological model of tomato sauce (Solanum lycopersicon) is a non-Newtonian and Herschel-Buckley type, considering appreciable initial shear stress for flow to occur, in which the rheological model is more functional describing the behavior and particulate states in the tomato sauce, fitting, as mentioned, very well to the Herschel-Buckley model.

Keywords: Compilation; Food engineering Rheological model

Introduction

One of the most commonly used and generally applied models to fix experimental data and quantitatively express the flow behavior of the inelastic time-independent fluids is the model proposed by Herschel Buckley given by the expression $\tau = K(\gamma)^n + \tau_0$; depending on the values of the constants, the model can be represented as non-Newtonian behavior, Bingham plastic, pseudoplastic or dilatant fluids [1]. Kleopatra et al., (2015) mention that rheological properties of wheat gluten have been evaluated with a rotational viscometer and so the rheological model is the one described by Ostwald which obeys Power Law by the expression $\tau = k\gamma^n$ [2]. It's also known that if a material gets deformed and has no flow when stress is applied, a solid material is obtained; if the material flows when a little stress is applied (in Mathematical terms: differential stress) so it's a fluid [3]. Cueto (2019) mentions that, in the rheology of the hydrocolloid of Ratanya (*Triumfetta semitriloba* jacq.) the evaluation of the behavior of time-dependent flow reveals a different tender getting a little thixotropy at low concentrations prevailed [4]. This tender is replaced by a remarkable anti-thixotropic behavior at intermediate concentrations (0.10 to 0.20%) to finally converge on a thixotropy fluid at higher concentrations than 0.2 % or between 12 and 18 °Brix, following

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a rheological model of Herschel-Buckley [5]. Gums and hydrocolloids are a unique category of food additives that provide a great number of desirable functional properties and important characteristics to the foods. These properties include soft textures, consistent rheological characteristics, stability of the finished product and possible heat reduction and modulation of the intestinal microflora [6]. Cardona-Palacio (2016) mentions that foods, apart from providing characteristic odor, color and flavor, show a specific mechanical behavior reacting in a certain way when it's intended to get them deformed. Moreover, they can be hard or tender, consistent or easily broken, gummy or breakable, uniform or fibrous texture and many other physical and chemical forms of presentation [7]. The results of different research suggest that some physicochemical properties, rheological factors such as the yield index and consistency factor of fruit juices, nectars, sauces and fruit syrups can be closely related to each other. Phinney, et al. (2017) mention that one of the foods mechanical behaviors consists of touching, squeezing, biting or chewing the food and describing the rheological sensations: sensorial method (physiological, psychological) so the ideas change from one analyst to another requiring a statistical and/or objective treatment [8]. The comparison of the rheological models based only on the Standard Error of Estimate (SEE) is not necessarily the best one as the SEE is relative to the magnitude of the values themselves, that is to say, the density, specific heat, thermal conductivity, viscosity and other thermophysical properties. To correct this, a relative standard value as percentage (%) can be found and medium values of coefficients in the individual expression turn into in coefficients in the models that have the standard error (%) of each model [9]. To solve the difficulty offered by the diversity of products (the almost infinite diversity of these that also have different properties), the rheologist takes reference points (patterns) constituted by ideal substances as the solids (steel, glass, rocks) that exhibit some proper characteristics of the liquids except one, the ideal solid that, by definition, lacks these properties; as well as there is a liquid that also lacks, by definition, any of the typical properties of the solids; the ideal liquid [5,10]. The viscosity is a transport property used in design and optimization of chemical and petrochemical processes that involve fluid transport, agitation, mixture, filtration, heat exchange and concentration [9]. The viscosity is a fundamental attribute to determine the quality of many foods both liquids and semisolids and, in some foods like ketchup, it is the most important attribute as it defines the acceptance by the consumer. Moreover, among the parameters that contribute to flow properties of ketchup, the quality of the raw material (maturity and variety of the fruit) and the conditions of elaboration processes stand out [10]. The non-Newtonian liquid is defined as the one for which the representation of the shear stress according to strain rate (or shear rate) is not necessarily a straight line [11]. For practical purposes, if the Déborah number is far less than the unit, it is a fluid; and if the Déborah number is much more than the unit, it is a solid [12]. Between the ideal solid and fluid there is an intermediate region where some materials behave as solids under certain conditions, but fluids under others (under the same pressure and temperature conditions) so the time when the process occur varies, materials are classified as viscoelastic and present a Déborah number of 0.6 order [13]. Regarding non-Newtonian liquids, it is said that in the apparent viscosity, flow is described by the equation $\tau = k \times D^n$, which means that tangential stress is not the same as shear stress. The representation of $ln\ \tau$ vs $ln\ D$ is a straight line that generally passes through the origin and the slope of this line is represented by n. As n is a constant, a determination is enough to completely characterize the behavior in the liquid flow. Ángeles (2018) mentions that in the food processing such as juices and nectars, as well as marmalades, sauces and syrups elaborated from fruits. The nutritional and sensorial properties are quite important, and among these, there are the rheological properties that correspond to an appropriate texture motivating the consumer to get interested and contributing the acceptance of the product [14,15]. The most used materials in the biodegradable sheets are the protein polysaccharides and lipids including starch, cellulose, alginate, gums, chitosan, pectin, casein, zein, gluten, keratin, albumin, wax and mineral oils; materials that alter the rheology of the products [16]. Marín-Machuca et al., (2021) mention that the rheology is defined as the study of the deformation and flow of matter; but this definition can be also expressed as the study of the relationship between the stress applied to a material and the deformation suffered by that material (for instance food materials) [17]. Identical techniques to the applied ones can be used sometimes for the rheological study of solid products, but it is evident that very low stress must be used for the study of the elastic behavior using the concentric cylindrical viscometer that allows to obtain the elastic modules and high viscosity values. Whorlow (2002) mentions that, in rheological terms, a plastic product flows when the stress exceeds a limit value, this elastic limit is denominated as stress of plastic deformation, τ_0; and that the ideal plastic product is the Bingham model where, for practical purposes, plastic substances are distinguished from the liquids as they do not flow when gravity is applied on them only [18]. Kobus et al., (2019) mention that the behavior of the non-Newtonian time-independent fluid can be better fixed to a plastic fluid of Bingham and that the rheological character of the liquid foods depends on several parameters such as the clarity, the content of soluble solids and extraction and preservation method such is the case with tomato sauce (*Solanum lycopersicon*) [19].

Materials and Methods

Procedure

All the rheological models are useful for the rheological characterization of the fluid products and all kind of foods. They can be performed and done based on mathematical models that express by an equation the relationship between the shear stress and (σ) and the velocity gradient (τ). The procedure consists of separating or classifying the foods into: 1) time-independent fluids which can be Newtonian fluids, non-Newtonian plastic fluids and non-Newtonian non-plastic fluids; and 2) time-dependent fluids which can be thixotropic and rheopectic.

Sample

Tomato sauce (Solanum lycopersicon) was obtained by collecting the raw material. The tomato was weighed and transported to a tray to get it washed. The process was performed according to the necessary requirements removing strange bodies (twigs, soil, leaves, etc.). The tomato was deposited in hampers from which it was taken to milling process putting in the whole tomato giving pieces not so small as a result. Afterwards, the pieces of tomato were taken to the pulper machine removing its seeds and rind obtaining tomato pulp. The pulp is taken to a weighing scale to measure the weight; then the evaporation process is performed concentrating tomato sauce. This concentration is measured in BRIX grades or Soluble Solid % (%S. S). In this opportunity, it was necessary to eliminate the excess of water through evaporation. Immediately, tomato sauce is transferred to marmite where sugar, salt and spices were added and mixed to obtain the expected characteristics according to the Royal Decree-Law 858 (1984). At the same time, pasteurization process was performed at 80 °C approximately for 20 minutes to avoid the proliferation of bacteria. Tomato sauce was packed in glass jars (previously sterilized) at 80°C being immediately closed and letting it get cold to create a vacuum environment which makes the product last longer. Tomato sauce (15 °Brix) (*Solanum lycopersicon*) was used by it is a nutritionally and functionally rich diet, as well as it allows to prevent illnesses such as cancer with almost exclusive substances mainly lycopene and other nutraceutical and even protein components. The benefits of the lycopene, carotenoid responsible for the red color of tomato, has attracted the attention due to its biological and physicochemical properties regarding the prevention of other chronic, cardiovascular, neurodegenerative illnesses and hypertension among others.

According to the Spanish Royal Decree-Law 858 (1984) it is understood that sauces are those food preparations because of the combination of different edible ingredients that, subjected to the convenient culinary treatment, are used to accompany food or food preparations. The sauce can be from liquid to smash in which elaboration, apart from raw matters that are specified in the definitions of each type of sauce, these can be used: sugars, starch, glucose syrup, gelatins, garlic, onion, and other vegetables, or its natural extracts, protein hydrolysates, vegetable proteins, eggs, ovoproducts, milk, vegetable oils, lemon juice, wine, vinegar, diverse spices and aromatic substances and any other ingredient authorized by "Dirección General de Salud Pública (General Direction of Public Health)" as this list has no restrictive condition.

Instruments, Equipment and Accessories. Among the equipment and instruments, we have those which only allow to obtain values of this relation $\sigma.\tau^{-1}$. The Haake Viscotester iQ Rheometer, Thermo Scientific Brand, Mooney – Ewart geometry (equipment used in this study). The capillary viscometer, consisting of a deposit, generally a U-shaped tube, where the fluid is poured. It is intended to measure the time a fluid takes to go through a determined capillary space. This time will be inversely proportional to the density and directly proportional to the viscosity. The constant of the instrument can be determined using fluids of known viscosities and so the size of the capillary tube must be selected according to the kind of fluid. If the capillary tube is too wide, the flow will be very fast and turbulent. If the capillary tube is too tight, the determinations will be very long, but quite accurate. [9] (709-711) Periods from 100 to 500 seconds offer a reasonable relationship between velocity and stress. The temperature must be controlled to be constant all time, as well as the verticality of the equipment and the strange bodies in the fluid that can affect the velocity of the fall. There are also rotational viscometers of infinite fluid (where there is a long distance between the recipient walls containing the fluid and the rotating rod), the tube viscometers and the rheometers. To measure °Brix of tomato sauce (Solanum lycopersicon), the MyBrix hand refractometer was used determining 15°Brix for the studied sample. This equipment is considered as perfect to measure any food and drink sample.

Characteristics and Specifications of the Product to be Elaborated

The determined rheological models are important to comprehend and understand the food raw matters as in the case of tomato sauce (Solanum lycopersicon). The obtained rheological models are valuably useful to comprehend the behavior of a food at the beginning, during and at the end of the technological process, and also in the final product. The rheological model obtained for tomato sauce (product obtained by partial evaporation of water restrained in the pulp and 15 °Brix) is a typical model of a non-Newtonian fluid in which the stress experimented by tomato sauce is related to the deformation of a complicated and non-linear way cauterizing, in this model, the consistency (k), the melt flow index (n) and yield stress (τ).

Results and Discussion

1. Having compiled the rheological models, which are described below, mentioning that they are the most important and for appliance to the rheological behavior of the foods, the following ones are listed:Casson Model. $\sigma^{0.5} = (\sigma_0)^{0.5} + K_1(\gamma)^{0.5}$

2. Modified Casson Model. $\sigma^{0.5} = (\sigma_0)^{0.5} + K_1(\gamma)^{n_1}$

3. Ellis Model. $\gamma = K_1\sigma + K_2(\sigma)^{n_1}$

4. Herschel-Buckley General Model. $\sigma = \sigma_0 + K_1(\gamma)^n$

5. Vocadlo and Parzonka. $\sigma = \left((\sigma_0)^{1/n_1} + K_1\gamma\right)^{n_1}$

6. Potencies series Model of Whorlow.

$$\gamma = K_1\sigma + K_2(\sigma)^3 + K_3(\sigma)^5 + K_4(\sigma)^7 + \ldots \sigma = K_1\gamma + K_2(\gamma)^3 + K_3(\gamma)^5 + K_4(\gamma)^7 + \ldots$$

7. Carreau Model. $\eta = \eta_\infty + (\eta_0 - \eta_\infty)[1 + (K_1\gamma)^2]^{(n-1)/2}$

8. Cross Model. $\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + K_1(\gamma)^n}$

9. Van Wazer Model. $\eta = \frac{\eta_0 - \eta_\infty}{1 + K_1\gamma + K_2(\gamma)^{n_1}} + \eta_0$

10. Powell and Eyring Model. $\sigma = K_1\gamma + \left(\frac{1}{K_2}\right) sen\, h^{-1}(K_3\gamma)$

11. Reiner Philippoff Model. $\sigma = \left(\eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + ((\sigma)^2/K_1)}\right)\gamma$

For all these rheological models, K_1, K_2, K_3 y n_1 and n_2 are arbitrary constants and power index respectively, all data is obtained in an experimental way.

Other rheological models can be described and applied

1. Tiu and Boger Model $\sigma = \lambda(\sigma_y + K\dot{\gamma}^n)$

Where K and n are the rheological constants that are determined at 0 time. It is said that the term λ is a parameter of structural rupture, function of the applied gradient velocity which depends on the time according to the kinetic equation of second order.

$$\frac{d\lambda}{dt} = k_1(\lambda - \lambda_c)^2$$

That, finding λ in the previous equation, deriving and replacing $\frac{1}{\sigma - \sigma_e} = (\sigma_0 - \sigma_e)^{-1} + at$n, the following equation is obtained:

Where a is related to k_1. From the data σ/t experimental to gradient of constant velocity, representing $(\sigma - \sigma_1)^{-1}$ to t, the value of k_1 can be obtained and allows to predict the value of λ at a given flow time.

1. Figoni and Shoemacker Model. These authors consider the simultaneous action of various structural fracture mechanisms of first order with different constants of velocity (k_i). At a constant of velocity gradient, the variation of yield stress according to time is given by the following

equation: $\sigma = \sum_i \sigma_{ei} + \sum_i(\sigma_{0i} - \sigma_{ei}) \times e^{-k_i \times t}$

In practice, the equation is applied with two terms of the summation being fixed to experimental data through non-linear fixing. The great mathematical correlation among the parameters complicates the analysis of the influence of gradient velocity on them.

Application

The rheological data (measured by Haake Viscotester iQ Rheometer) for tomato sauce (*Solanum lycopersicon*) are plotted in Table 1. *The behavior of the rheological data of tomato sauce (Solanum lycopersicon) according to the temperature is shown below (Figure 1). Plotting the experimental data and observing the behavior of the experimental data, it is concluded that the experience follows the general model of Herschel-Buckley, whose expression is this:* $\sigma = \sigma_0 + K_1(\gamma)^n$*; where* σ_0 *is the elastic limit,* K_1 *is the consistency coefficient and* n *is the melt flow index. Evaluating the rheological parameters correspondent to each temperature, the following rheological models (Herschel-Buckley) are obtained:*

- For $T = 5\,°C$: $\tau = 62 + 0.80727 \times \gamma^{0.810331}$ with $r^2 \times 100 = 0.99541$
- For $T = 10\,°C$: $\tau = 36 + 1.10930 \times \gamma^{0.74030}$ with $r^2 \times 100 = 0.97275$
- For $T = 20\,°C$: $\tau = 24 + 1.22636 \times \gamma^{0.69755}$ with $r^2 \times 100 = 0.98273$
- For $T = 30\,°C$: $\tau = 14 + 0.514206 \times \gamma^{0.8010}$ with $r^2 \times 100 = 0.98830$
- For $T = 40\,°C$: $\tau = 8 + 0.23106 \times \gamma^{0.878426}$ with $r^2 \times 100 = 0.98234$
- For $T = 50\,°C$: $\tau = 3 + 0.203656 \times \gamma^{0.84970}$ with $r^2 \times 100 = 0.98851$
- For $T = 60\,°C$: $\tau = 2 + 0.13566 \times \gamma^{0.8366244}$ with $r^2 \times 100 = 0.98431$

Whereby the values of the consistency coefficient (K_1*) and the melt flow index (*n*) are respectively obtained and summarized in the Table 2.*

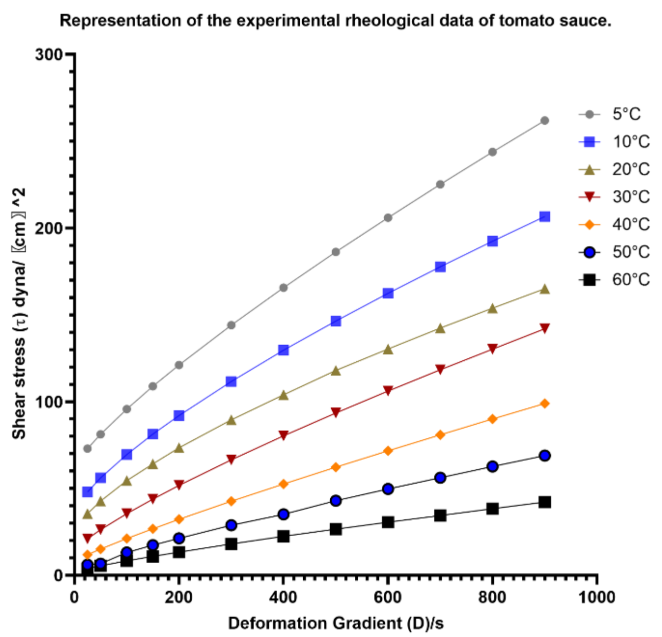

Figure 1: Plot of the experimental rheological data of tomato sauce (Solanum lycopersicon).

Table 1: Rheological data for tomato sauce (Solanum lycopersicon) according to the temperature.

	TEMPERATURE						
	5°C	10°C	20°C	30°C	40°C	50°C	60°C
D	τ	τ	τ	τ	τ	τ	τ
25	72.96	48.02	35.58	21.02	11.92	6.14	4.00
50	81.22	56.08	42.80	26.30	15.18	6.67	5.58
100	95.70	69.55	54.6	35.54	21.20	13.20	8.40
150	108.91	81.30	64.2	43.92	26.85	17.40	10.97
200	121.10	92.04	73.52	51.80	32.27	21.37	13.42
300	144.09	111.66	89.52	66.51	42.65	28.90	18.05
400	165.65	129.62	104.00	80.30	52.61	35.10	22.50
500	186.19	146.43	118.02	93.45	62.30	43.01	26.60
600	205.96	162.39	130.30	106.10	71.70	49.72	30.62
700	225.11	177.67	142.40	118.36	80.93	56.26	34.42
800	243.75	192.39	153.92	130.29	90.01	62.67	38.41
900	261.96	206.64	165.04	142	98.95	68.94	42.20

D: (s^{-1}); τ: (dina cm^{-2})

Table 2 :

Temperature, T (°C)	Consistency Coefficient, K_1	Melt Flow Index, n
5	0.80727	0.810331
10	1.10930	0.740300
20	1.22636	0.69755
30	0.51421	0.80100
40	0.23106	0.878400
50	0.20366	0.849700
60	0.13566	0.836600

Data of the consistency coefficient (K_1) and the melt flow index (n).

Figures, Tables and Schemes

The standard Error of Estimate (SEE) for the consistency coefficient (K_1) and the melt flow index (n) were respectively 0.3556 and 0.0587 whose relative standard value and the individual coefficients of the models turn into constituent coefficients with the standard error of each model agreeing with Phinney, et al. (2017). The obtained results regarding the melt flow index (capacity of a liquid food to displace in laminate state

after heat and pressure submission) and consistency coefficient (that is the strength per surface unit required to move a fluid at a stablished cutting speedy or minimum required strength to move a fluid) satisfactorily agree with the one reported by Alvis et al. (2016). The rheological behavior of tomato sauce (Solanum lycopersicon) follows the Herschel-Buckley rheological model agreeing with Kokini (1992), Marín-Machuca et al. (2021), Cueto (2019) and Rydzak et al., (2020). The values of the elastic limit graphically evaluated are not significantly different from the ones evaluated by the statistical or mathematical model according to Whorlow R. W. (2002) y Rydzak et al. (2020).

Conclusion

It is concluded that the tomato sauce (15 °Brix) presents a strong structure and thixotropic behavior and that the structural parameters allow inferring the incidence of the composition and the shear rate on the structure of the sauce. It is concluded that the rheological models are quite important and versatile in the foods and the food processes describing variable behaviors. They are as complex as can be imagined. Likewise, the rheological models have to be meticulously and firmly treated which requires an advanced Statistics and Mathematics. Many of the rheological models require topological and tensor concepts, analysis of matter deformation, food elasticity, among other disciplines. To evaluate rheological parameters of the food and other substances or food materials, it is required to design sophisticated equipment and instruments of measurement. We proposed the pertinent recommendations (to understand and predict the rheological behavior of the foods) such as being fully informed about advanced Mathematics and Statistics, experimental models in processes and differential equations. Preferably, it is necessary that the equipment and instruments of measurement be calibrated as well as evaluate the parameters or tests as much carefully as possible and the temperature and concentration which the experiences are at must be constant through all the measurement process. The applications that can be performed are diverse and multiple in the liquid foods industry. We can mention the tropical fruit-based yogurt, wild fruit-based nectars and shakes based on ovine milk, etc.

Author Statements

Conflict of Interests

The authors declare that they have no conflicts of interest.

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