MATHEMATICAL MODELLING AND THE DETERMINATIONOF ACTIVATION ENERGY AND MOISTURE DIFFUSIVITY EFFECTIVENSS OF GLASS SHRIMPS (*PALAEMONETES PALUDOSUS*)

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ABSTRACT

Glass shrimp (Palaemonetes paludosus) tends to degrade after harvest due of high systemic moisture associated with it. To reduce degradation and enhance quality glass shrimps, convectional drying method was employed under six different temperatures, ranging from 50 - 100°C in multiples of 10°C. The dehydration values were inserted into about seven thin layer model; namely Henderson-Parbis, Page, Midilli, Newton, Logarithmic, Two-Terms, and finally Diffusion Approximation model to predict glass shrimp. The mechanism of these models was assessed using coefficient of determination (R^2), reduced chi-square (X^2) and root mean square error (RMSE). The emanating drying constants and coefficients, activation energy and moisture diffusivity effectiveness were investigated using a non-linear regression statistical conceptualization and linearized Fick's second law equation method. Midilli model was the best models applicable for predicting the drying behaviour of the glass shrimp. The temperature dependent effective diffusivity values ranged from $1.85 \times 10^{-9} – 2.95 \times 10^{-9}$-$m^2/s$ with the related activation energy value of 30.5kJ/mol

Key words: Glass Shrimp, Drying Kinetics, Thin Layer, Activation Energy, Moisture Ratio, Effective Moisture Diffusivity.

INTRODUCTION

Glass shrimp (Palaemonetes paludosus) also called ghost shrimp is a variety of freshwater shrimp that can be found in most coastal area of south-south Nigeria. In Nigeria, dried shrimp is also known to be an important fishery product and its colour, size, dryness, and taste all influenced the price of shrimp during sales.

Although natural sun drying is a low-cost processing method, it has drawbacks including the inability to regulate the drying process and its variables, unpredictable weather conditions, a large drying space, a high risk of insect, and contamination from external substances and impurities (Jain and Pathare, 2007). Shrimp drying is typically done by boiling the shrimp in salt water and then sun drying for three to five days (Jain and Pathare, 2007)

In addition to being a high-potential source of animal protein, glass shrimp by-products are also a good source of chitin and asthaxanthin as reported by (Shahidi and Synowiecki, 1991). Shrimps can be preserved in many different ways, such as drying, freezing and cannin (Rungtip et al., 2005; Lourdes et al., 2007). Shrimp can be preserved using canning or freezing in modern economic, drying is the preferred option in developing nations like Nigeria since it's more affordable when compared to freezing and canning.

The removal of moisture from moisture systemic food and air requires an elaborate process that involves simultaneous transmission of mass and heat. The drying kinetics analyses are used to predict how food products will behave during drying. To optimize drying system working conditions, mathematical models that characterize the drying process are used (Latiff *et al.,* 2021)

Food, particularly aquatic products, degrade rapidly, to prevent deterioration and extend the shelf life of foods, drying techniques are employed. The following are a few examples of drying experiments with various meat products: Egbe and Zibokere, (2021) investigated drying kinetics of fresh-water crayfish and Burubai and Bratua, (2016) fresh water frog.

Furthermore, the majority of glass shrimps are dried by spreading them out on a mat under the direct sun (Rungtip *et al.,* 2005, Nwanna *et al.,* 2004). Glass shrimps tends to deteriorate immediately harvested which has led to scarcity and increased in price in market places especially during off-seasons. This problem necessitates the creation of a better and more effective drying technique capable of prolonging the shelve of glass shrimps. This can be accomplished by figuring out how much energy is needed to dry the samples by studying the glass shrimps' drying behavior. The objective of this research work is to determine the activation energy and moisture diffusivity effectiveness of glass shrimps using Fick's law of diffusion and to adjust the results of the experiment into seven different mathematical models in other to choose the most appropriate model for forecasting the drying kinetics of glass shrimp.

Materials and Methods

Sample Preparation and moisture content determination

For the study, a sizable quantity of live Glass shrimp (Palaemonetes paludosus) were procured from the Ondewari community in the Southern Ijaw Local Government Area of Bayelsa State, Nigeria. The samples were delivered to the Niger Delta University, Food Processing Laboratory in Bayelsa State, Nigeria, which is part of the department of agricultural and environmental engineering. They were rinsed in brine water and given the opportunity to rest in fresh saline water (brine) in the comfort of the laboratory for 30 minutes. This ensures that salt osmotic penetration is consistent across all samples. For preservation, the cleaned and pre-osmosed samples were placed in transparent poly-bags and kept in a refrigerated cabinet. Using a top digital balance, eighteen (18) sets of 7-g specimens were extracted from the samples. Each sample in each set of specimens had its initial moisture content determined. The specimens were then oven dried in a WTC binder oven (Model WTCB 1718) at temperatures of 50, 60, 70, 80, 90, and 100°C. Each set of specimens was dried to a constant final weight and replicated three times for each temperature level, with the average value recorded for each using a laboratory-style top digital balance with 0.01-g precision, all weight measurements were recorded according to ASAE (2000) standard method. The final moisture content for each replicate was calculated using the weight differences, all measured on dry-basis as in equation 1

$$M = \frac{w_i - w_f}{w_f} \qquad \ldots \qquad 1$$

where

M = dry basis moisture content, %-db, W_i = initial weight of the specimen, g, W_f = final weight of the specimen, (g)

Strong evidence from pertinent literature suggests that biomaterials are dried during a period of declining rate (Brennan et al., 1969; Toledo, 2000; Earle, 2006;). Equation 2 from Bird et al. (2005) shows that the Fick's second law governs molecular transport (diffusion) through a continuum of thin interface layers.

$$\frac{dM}{dt} = D_e\left(\frac{d^2M}{dr^2}\right) \qquad \ldots \qquad 2$$

For several thin spherical layers, the analytical solution of (2) can be (Ndukwu and Karen, 2011)

$$MR = \frac{6}{\pi^2} e^{-nD_e t\left(\frac{\pi}{r}\right)^2} \qquad \ldots \qquad 3$$

Taking natural log on both sides

$$\ln(\mathrm{MR}) = \ln\frac{6}{\pi^2} - nD_e\left(\frac{\pi}{r}\right)^2 t \quad \ldots \qquad 4$$

After that, effective diffusivity, De, can be calculated from the slope of the plot of drying time, t, and ln(MR). This can be inferred from the slope De as

$$\mathrm{De} = \frac{Slope\ of\ plot\ [r^2]}{n\pi^2} \quad \ldots \qquad 5$$

The moisture ratio in this context can be (Sahay and Singh, 2005),

$$\mathrm{MR} = \frac{\mathrm{M} - \mathrm{M_e}}{\mathrm{M_o} - \mathrm{M_e}} \quad \ldots \qquad 6$$

$$\mathrm{MR} = \frac{\mathrm{M}}{\mathrm{M_o}} \quad \ldots \qquad 7$$

Activation Energy

This quantity of energy is necessary for the initiation of moisture transfer during the drying of biomaterials with a high bound water content. The activation energy in diffusion is determinable using a relationship of the Arrhenius type. (Burubai, 2016).

$$D_e = D_o(e^{-E_a/Rt}) \quad \ldots \qquad 8$$

Simplification of (8) gives

$$\ln D_e = \ln D_o - \frac{E_a}{Rt} \quad \ldots \qquad 9$$

where in $$E_a = \ln\left(\frac{D_o}{D_e}\right)Rt \quad \ldots \qquad 10$$

The linear plot of lnDe against t^{-1} has an intercept of lnDo at the InDe axis, and the slope of this plot, Ea/R, corresponds to the activation energy of glass shrimps.

Thin Layer Mathematical Drying Models

In technical literature, mathematical models are frequently used to predict the way biomaterials including those from agriculture behave as they are been dried. Table 1 shows a variety of thin-layer drying models used in the work.

Table 1: Mathematical drying models

MODELS	EQUATIONS	REFERENCES
Henderson and Pabis	MRexp= aexp(-kt)	Henderson and Pabis, (1961)
Midilli	MRexp = aexp(ktn)+bt	Midilli et al.,, (2002)
Newton	MRexp = exp(-kt)	Kingly et al.,, (2007)
Page	MRexp = exp(-kt^n)	Vega-Gálvez, (2010)
Logarithms	MRexp = aexp(-kt) +c	Akpinar, (2008)
Two-Terms	MRexp = aexp(k_1t)+b exp(k_2t)	Hodge & Taylor, (1999
Diffusion Approximation	MRexp = aexp(k_1t)+(1-a) exp(kbt)	Sacilik et al.,, (2005)

Obtaining Drying Curves

When it comes to thin layer drying, controlling drying rates is essential, to reduce drying time, increase the drying rate at different drying temperatures. However, drying materials with a lot of body moisture under a variety of drying conditions at high temperatures (like above 80°C) might not produce the best results (Shi et al., 2008, Chen et al., 2013). The amount of moisture that is removed during drying can be predicted by the cubic polynomial form of the drying time in the direction of Y for a given split and a given drying temperature (Hayder et al., 2014)

$$y = C_0 + C_1 t + C_2 t^2 + C_3 t^3 + C_4 t^4 \qquad 11$$

$$\frac{dy}{dt} = -(c_1 + 2c_2 t + 3c_3 t^2 + 4c_4 t^3 \ldots) \qquad 12$$

The negative sign denotes a decline in drying rate as drying time passes. Eq. 12 can be simplified to: if higher powers of t are regarded as negligible.

$$\text{Drying rate}\left(\frac{dy}{dt}\right) = -(c_1 + 2c_2 t + 3c_3 t^2 \ldots) \qquad 13$$

Eq. 13 generates drying curves for the various drying temperatures used in this study, which can be plotted on a drying rate vs. drying time graph.

Statistical Fitting of Experimented Data

Utilizing the (r^2), (X^2), and (RMSE) statistical techniques, the tested mathematical model's capacity to represent experimental data was evaluated. The criteria state that the model's ability to predict is improved by having a r^2 value that is near 1, as well as an RMSE and X^2 value that are close to 0. (Wang et al., 2007). The parameters listed above the statistical parameters used in the calculation of the indicators as described and their mathematical definitions are as follows:

$$r^2 = 1 - \left[\sum_{i=1}^{n} (MR_{pre,i} - MR_{exp,i})^2\right] \quad \ldots \quad 14$$

$$\chi^2 = \frac{\sum_{i=1}^{n} (MR_{pre,i} - MR_{exp,i})^2}{n - k} \quad \ldots \quad 15$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} (MR_{pre,i} - MR_{exp,i})^2}{n}} \quad \ldots \quad 16$$

Results and Discussions

Drying Kinetics

The drying curves in Figures 1 and 2 are based on the information gathered from the sample data. As drying time increased, Figure 1 demonstrates that the samples moisture ratio dropped (increased drying). For such a bio-product with a high content of bound water, fats, oils, and proteins, the drying curves' slow tangential approach to the drying time axis suggested that the transport of moisture from the core to the surface for evaporation was rather slow. This suggests that the drying process did not take place during a constant rate period but rather during a falling rate period. The slow pattern of the drying curves also demonstrated that even at high temperatures, drying took place lacking case-hardening.These findings are consistent with previous research on mud snail by Burubai and Bratua, (2015), tilapia by Zhiqiang , (2013), catfish by Sankat and Mujalfar, (2008), and clams by (Burubai, 2015). The plot exponential drying curves suddenly dropped sharply see (Fig. 2) indicated that drying occurred primarily during the falling rate period. This is related with reports on the thin layer drying of yoghurt (Hayaloglu *et al.*, 2007), potatoes (Akpinar *et al.*, 2003), bananas, (Ganesapillai *et al.*, 2011), plantain (Satimehin and Alabi, 2005), pumpkin seeds (Jattanit, 2011), fresh fish (Kilic, 2009), tomatoes (Kross *et al.*, 2004) and bitter kola (Ehiem and Simonyan, 2011).

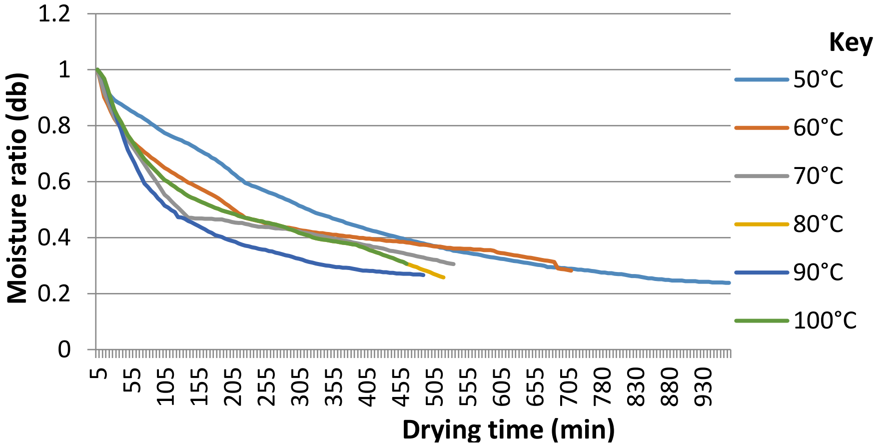

Fig. 1: Drying curve at different temperature for Freshwater Glass Shrimps

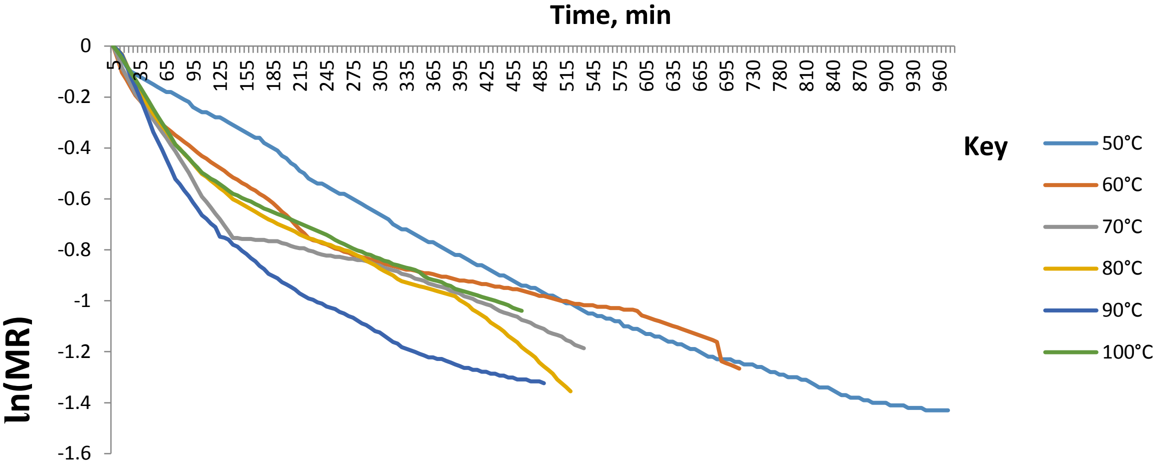

Figure 2: Drying curve of freshwater *Glass shrimp (Palaemonetes paludosus)*

Fitting Experimental Data into Drying Models

The results from the experimental drying were modeled using seven thin layer drying models namely Henderson-Parbis, Page, Midilli, Newton, Logarithmic, Two-Terms, and finally Diffusion Approximation model. This is to allow for the selection of the model that best describes the kinetics of glass shrimps. The data were first fitted into the Ficks diffusion equation (eqn. 2) using the approach of non-linear least square statistic of SPSS (1996) to satisfactorily obtain constants ‘a’ and ‘k’. Values obtained were then statistically predicted using (r^2), (RMSE). As shown in Fig. 3, the experimental and experimented MR values were plotted and regressed using the reduced chi-square (2). The results are presented in Tables 2. To explain the drying characteristics of the glass shrimps, the model with the lowest RMSE, and highest r^2 was chosen as the best fit model. It can be seen that of the seven models applied in this work, the Midilli model gaves the lowest RMSE and χ^2, and highest r^2 values and is accordingly accepted as representing the dry characteristics of the glass shrimps.

Table 2: Statistical Parameters of Fresh Water *Glass shrimp (Palaemonetes paludosus)* on Seven Selected Thin-layer Drying Models.

MODEL	Temp °C	Constant and coefficients	R^2	RMSE	X^2
Henderson and Pabis	50	a= 0.983, K= 0.532	0.9543	0.42750	0.3456
	60	a= 0.989, k=0.538	0.8533	0.54830	0.2357
	70	a= 0.994, K = 0.623	0.9583	0.56440	0.3125
	80	a= 0.996, K= 0.648	0.9875	0.34420	0.1753
	90	a= 0.9988, K=0.655	0.9654	0.32160	0.1694
	100	a=1.002, K=0.689	0.9457	0.23650	0.1642
Midilli	50	k =0.324, a=1.234 , b= -0.012, n=1.943	0.9999	0.00014	0.0032
	60	k = 0.321, a= 1.211, b=- 0.019 , n=1.912	0.9999	0.00043	0.0043

	70	k =0.234, a= 1.204, b= -0.015, n= 1.832	0.9999	0.00070	0.0020
	80	k =,0.214 a= 1.134, b=-0.012 , n= 1.742	0.9999	0.00015	0.0052
	90	k =0.143, a= 1.208, b=- 0.001, n= 1.632	0.9997	0.00021	0.0024
	100	k =0.122, a= 1.114, b=-0.006 , n= 1.521	0.9998	0.00012	0.0066
Newton	50	k= 0.534	0.9992	0.02353	0.0125
	60	k= 0.586	0.9984	0.02345	0.0153
	70	k= 0.632	0.9866	0.03574	0.0168
	80	k= 0.654	0.9889	0.02269	0.0194
	90	k= 0.744	0.9992	0.03421	0.0186
	100	k= 0.932	0.9993	0.02689	0.0195
Page	50	k= 0.988, n= 1.984	0.9994	0.01284	0.0146
	60	k= 0.978, n= 1. 864	0.9979	0.01065	0.0158
	70	k= 0.594, n= 1.763	0.9977	0.01467	0.0179
	80	k= 0.546, n=1.567	0.9991	0.01654	0.0158
	90	k= 0.532, n= 1.453	0.9976	0.01876	0.0118
	100	k= 0.512, n=1.324	0.9971	0.01326	0.0143
Logarithmic	50	a= 0.121, a= 3.065, b= -2.965	0.9923	0.04320	0.0032
	60	a= 0.115, a=3.024, b= -2.853	0.0994	0.03420	0.0030
	70	a=0.110, a=2.074, b= -2.753	0.9991	0.03210	0.0023
	80	a=0.103, a= 2.032, b= -2.648	0.9992	0.02450	0.0021
	90	a= 0.094, a= 1.063, b=-2. 538	0.9997	0.02670	0.0018
	100	a=0.083, a=1.030, b= -2. 417	0.9993	0.04430	0.0012
Two-Term	50	a=0.943, b=0.985, k_1= -0.432, k_2 = -0.485	0.9456	0.00321	0.0016
	60	a=0.932 , b=0.953 , k_1=- 0.523, k_2 = -0.534	0.9345	0.00321	0.0013
	70	a=0.753 , b= 0.942, k_1=-0.613 , k_2 = -0.632	0.9655	0.00323	0.0019
	80	a= 0.643, b= 0.935, k_1= -0.718, k_2 = -0.735	0.9654	0.00243	0.0018
	90	a=0.543 , b= 0.926, k_1= -0.724, k_2 = -0.789	0.9654	0.00213	0.0017
	100	a=0.453 , b= 0.912, k_1= -0.805, k_2 = -0.825	0.9487	0.00245	0.0020
Diffusion Approximation	50	a = 0.121, b = 0.447, k = 1.372	0.9924	0.00467	0.0056
	60	a = 0.097, b = 0.411, k= 1.333	0.9992	0.00543	0.0043
	70	a = 0.026, b = 0.334, k= 1.077	0.9994	0.00653	0.0054
	80	a = 0.019, b = 0.176, k = 1.104	0.9991	0.00457	0.0087
	90	a = 0.016, b = 0.156, k = 1.121	0.9993	0.00658	0.0043
	100	a = 0.014, b = 0.146, k = 1.110	0.9994	0.00453	0.0032

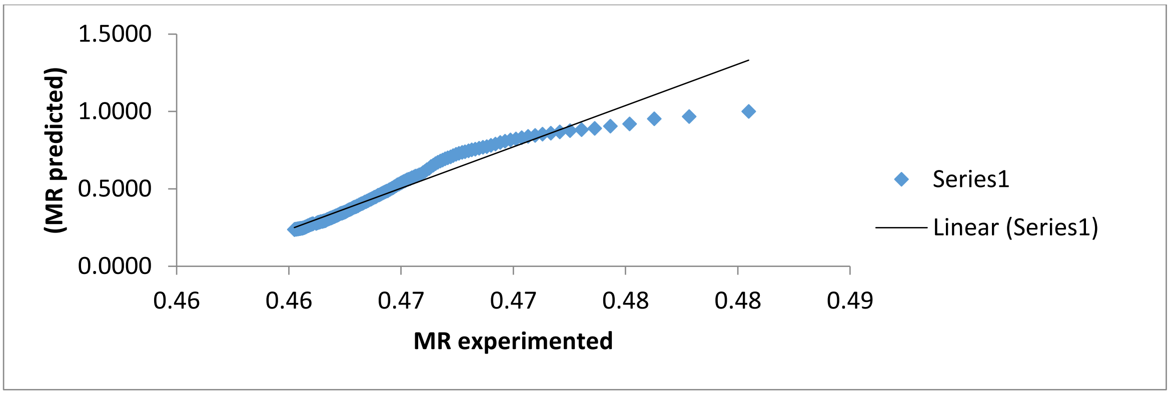

Fig. 3: Relationship between MR experimental and MR predicted values.

Effective Diffusivity (D_e)

On three replicates of each of the temperatures used in this study, effective diffusivity, De, was calculated to be ranging from 1.85 x 10^{-9} – 2.95 x 10^{-9}-m^2/s using Equations 2 to 5. The values show that moisture diffusivity (or otherwise defined as moisture migration from thin layer protein-base solid matrix to the surface of the glass shrimps) increased as temperature increased. This makes sense because the drying process relies on a diffusion mechanism that is thought to work in response to applied energy levels. This supports the claims made by Burubai and Bratua (2015) on mud sails and Sacilik (2007) on pumpkin seeds.

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Activation Energy, E_a

This is a measurement of the glass shrimps heat sensitivity when dried. It is a temperature-dependent moisture transport parameter that was obtained by linearizing the Arrheneus type equation (eqns. 8 through 10) using the graphical method shown in Figure 4 for the various temperature levels used in this study. The greater the Ea, the longer it will take to dry to the specified moisture content level (dry basis). The average value of Ea in this study was 33.5 kj/mol. This finding is between the range of 12.7kj/mol for high moisture biomaterials and 0.53kj/mol for low moisture, diffusion controlled biomaterials (Zogzas *et al.*, 1996).

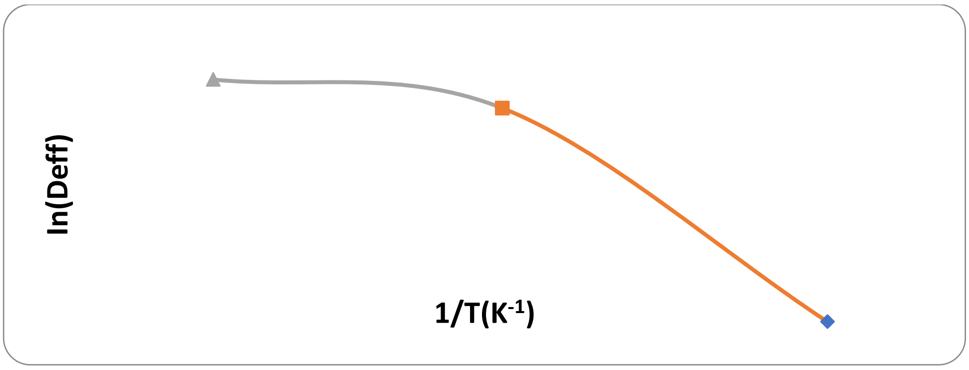

Figure 4: Estimation of Activation Energy for *Glass shrimp (Palaemonetes paludosus)*

Conclusion

The drying kinetics of glass shrimps were studied and it became clear like other biological materials as the drying process belongs to the falling rate period. The Midilli model which had an effective moisture diffusivity ranging from 1.85 x 10-9 to 2.95 x 10-9-m2/s over the temperatures used in the work was the most effective at predicting the drying kinetics of glass shrimps among the seven thin layer models that were investigated. The corresponding activation energy value was 30.5 kJ/mol.

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