# Shelf-life study of co-milled carrot with fermented quality protein maize (QPM) using sorption isotherm

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**Abstract**

*Shelf-life of a food product is the time, it stays qualitatively acceptable and safe for consumption. One of the methods of estimating shelf-life of food is by the use of food sorption isotherm. This study is aimed at determining effect of varietal difference on the shelf-life of co-milled carrot and fermented maize (ogi) flour using BET monolayer model. Two samples of maize varieties; a yellow colored (TZE-YPOP-DT-STR-QPM) variety was studied in comparison with yellow coloured normal maize (SUWAN-ISR). These were co-milled separately with 40% carrot. Adsorption isotherm was used to determine the shelf life of the co-milled flour samples at room temperature over a range of water activities ($a_w$) of 0.1 to 0.8. The result for 20CMN and 20CMQ showed that Equilibrium Moisture Content (EMC) increases with $a_w$ (1.50-10.87 and 1.57-10.52, respectively) at room temperature. Also, amount of water absorbed which is directly proportional to EMC increased with increased water activity. Sample 20CMQ absorbed more moisture than sample 20CMN at low water activity (between 0.1- 0.5) and vice-versa at $a_w$ above 0.5. Incidentally, the estimated BET monolayer for 20CMN (3.43) is lower than 3.52 obtained for 20CMQ. It is established that at high relative humidity, flour from normal endosperm maize will deteriorate faster than that of QPM flour, meaning that the shelf-life of QPM flour will be longer than that made from normal endosperm.*

**Keywords:** shelf-life, desorption, water activity, co-milling, maize - *ogi*

## Introduction

The shelf life of food is the period during which the food retains an acceptable quality from a safety and organoleptic point of view, and depends on four main factors, namely formulation, processing, packaging and storage conditions (Yuthana and Panuwat, 2016) and may vary from a few days to several days or years (Timmermann, 2001). An important factor in the loss of quality of dried foods during storage is the water activity (aw) which influences the biochemical reactions such as lipid oxidation, caking, agglomeration and degradation of vitamins and lycopene (Akanbi and Oludemi, 2003). The Quality Protein Maize (QPM) is a distinct species among the cereals because of the presence of high amount of two essential amino acids viz., lysine and tryptophan and low content of non-desirable amino acid (leucine) in it. Therefore, it can be utilized for diversified purposes in food and nutritional security as infant food, health food/mixes, convenience foods, specialty foods and emergency ration (TASS, 2008).

The food sorption isotherm describes the thermodynamic relationship between water activity and the equilibrium of the moisture content of a food product at constant temperature and pressure. The knowledge and understanding of sorption isotherms has been highly helpful in Food Science and Technology for the design and optimization of drying equipment, design of packages, predictions of quality, stability, shelf-life and for calculating moisture changes that may occur during storage. The typical shape of an isotherm reflects the way in which the water binds the system. Weaker water molecule interactions generate a greater water activity, thus, the product becomes more unstable.

Sorption isotherms can be generated from an adsorption process or a desorption process; the difference between these curves is defined as hysteresis, as it is shown in Figure 1. Water adsorption by food products is a process in which water molecules progressively and reversibly mix together with food solids via chemisorption, physical adsorption, and multilayer condensation. An isotherm can be typically divided into three regions; the water in region A represents strongly bound water, and the enthalpy of vaporization is considerably higher than the one of pure water.

The bound water includes structural water (H-bonded water) and monolayer water, which is absorbed by the hydrophilic and polar groups of food components (polysaccharides, proteins, etc.). Bound water is unfreezable and it is not available for chemical reactions or as a plasticizer. In region B, water molecules bind less firmly than in the first zone, they usually present in small capillaries. The vaporization enthalpy is slightly higher than the one of pure water. This class of constituent water can be looked upon as the continuous transition from bound to free water. The properties of water in region C are similar to those of the free water that is held in voids, large capillaries, crevices; and the water in this region loosely binds to food materials (Kinsella, 1976).

Moreover, hysteresis is related to the nature and state of the components of food, reflecting their potential for structural and conformational rearrangements, which alters the accessibility of energetically favourable polar sites. The presence of capillaries in food results in considerable decrease in water activity. The explanation for the occurrence of moisture sorption hysteresis comprises the ink bottle theory, the molecular shrinkage theory, the capillary condensation, and the swelling fatigue theory (Raji and Ojediran, 2011). Moisture sorption isotherms show in graphical form the variation in water activity (aw) with change in moisture content of a sample at a specified temperature (Rahman, 1995). Samapundo *et al*. (2007) determined the adsorption and desorption isotherms of yellow dent corn at 25, 30 and 37$^0$C. The moisture isotherms for yellow dent corn have been found to exhibit Type II behaviour and to be temperature dependent as the equilibrium moisture content decreases with increase in temperature (Samapundo *et al*., 2007).

A number of models, mostly semi-empirical and empirical, have been attempted to be fitted to maize and maize products moisture isotherms over a wide range of water activity (Al-Muhtaseb *et al*., 2004), and yellow dent corn (Samapundo *et al*., 2007) in particular. The genetic modification which gives rises to QPM variety is likely to have altered the arrangement of the water constituents; free and bond water. Also little information is available on shelf- life study of ogi flour using sorption Isotherm, so the need for this study. Therefore this study is aimed at determining effect of varietal difference on the shelf- life of co-milled carrot and fermented maize (ogi) flour using BET monolayer model.

## Materials and methods

### *Experimental materials*

Two samples of maize varieties were studied; a yellow coloured QPM variety was studied in comparison with yellow coloured normal maize variety. The QPM variety: TZE-YPOP-DT-STR-QPM was obtained from International Institute for Tropical Agriculture (IITA), Ibadan while the normal maize; SUWAN-ISR was obtained from Institute for Agricultural Research and Training (IAR and T), Ibadan. Intact whole seeds were picked manually and stored at refrigeration temperature prior to further investigations.

### *Production of co-milled flour blends*

Co-milled carrot/ogi flour was produced following the production of ogi (Oladeji *et al*., 2014) but with the inclusion of carrot on the production line. Carrot (40%) was added after the maize had been fermented, at the point of milling. The samples; 40% carrot co-milled with quality protein maize is coded 20CMQ while 20% carrot co-milled with normal maize is coded 20CMN.

*Determination of Moisture Sorption Isotherm*

Adsorption isotherm was used to determine the shelf life of the co-milled flour samples at room temperature

*Preparation of water activity solution*

Tetraoxosulphate (VI) acid has been used in sorption isotherm studies by other researchers (Peng *et al*., 2007). This is because it exerts no appreciable vapour pressure and undergoes no changes of importance during storage and use. Thus concentrated aqueous sulpuric acid was used to maintain the desired water activities. The concentrated tetraoxosulphate (VI) acid (% wt, 98; S.G., 1.84; MW, 98.07) was preferred because homogenous solution varying from 0-100% relative humidity can be obtained. The vapour pressures of these solutions have been as accurately determined as those of any other concentrated solution and they come to equilibrium rapidly with the surrounding atmosphere.

Eight different percentages of relative humidities ranging from 10-80% were employed at the temperatures 30 ± 2 $^{o}$C. To obtain the desired relative humidity conditions the concentrated aqueous tetraoxosulphate (VI) acid were prepared to different concentration values using water partial pressure (bar) over aqueous tetraoxosulphate (VI) acid data of Perry and Green (1984) and Mertz (1965). About 250 ml of each of the prepared relative humidity solution was transferred to a labeled flat bottom glass dessicator (250 mm diameter and 350 mm deep in base) with a perforated porcelain plate. Heavy oil was used to exclude the air entering through the edge. Vaseline was specifically used to prevent it flowing to the sample.

*Determination of sorption isotherms*

Wink's weight equilibrium method was used to determine the equilibrium moisture content of the sample at room temperatures (30$^{0}$C). Duplicate samples each of 2 g ± 0.001 g sufficient to give a uniform single layer were placed in Petri dishes which were placed inside sorption jars, which were at eight different atmospheres ($a_w$ = 0.1 to 0.8). The jars (desiccators) were placed on the shelf to maintain a room temperature (assume to be 30$^{0}$C). The weight of dry matter was determined by drying at 70$^{0}$C, 90 mm Hg for 8 hours. The equilibrium moisture content (EMC) of the samples was then determined by calculation from the original dried weights and the known change in weight. The absorption isotherm curves were obtained by plotting the EMC of the food samples (% dry weight basis) against the corresponding water activities ($a_w$). Since GAB model, had been proved by many researcher to be the best-fit model for many food materials in general over a wide range of water activity (Timmermann *et al*., 2001; Al-Muhtaseb *et al*., 2004), and yellow dent corn (Samapundo *et al*., 2007) in particular. GAB model was used as modelling of adsorption isotherms of the samples while BET model was used to determine the monolayer moisture content of each sample.

*Calculation of Monolayer Value (Mo) using BET Equation*

The monolayer value (Mo) was calculated using BET equation as shown below;

$$\frac{aw}{M(1-aw)} = \frac{1}{MoC} + \frac{(C-1)}{MoC} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Let S = slope, I = intercept

Linearising the BET equation

$$S = \frac{C-1}{Mo-C} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$I = \frac{1}{MoC} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

By substitution

$$MoC = \frac{1}{I} = \frac{C-1}{S}$$

(C-1)I = S

$$C = \frac{S}{I} + 1$$

$$\frac{1}{Mo} = I\left(\frac{S}{I} + 1\right)$$

$$Mo = \frac{1}{S+I}$$

**Results and discussion**

*Adsorption Isotherms of co-milled samples*

The adsorption isotherms of co-milled flour samples at room temperature ($30\pm2^0$C) are shown in Figure 3. The adsorption isotherms have a sigmoidal shape showing an increase in the equilibrium moisture content (EMC) with water activity ($a_w$). Adsorption of water can be ascribed to the basic components of foods such as polymeric materials, proteins, starch and soluble solids e.g. sugars at high moisture contents (Kumar *et al*., 2005). The sigmoidal-shaped curve of the isotherms obtained in this study represents Type II isotherms, according to earlier reports (Bell and Labuza, 2000; Akanbi *et al*., 2006). This has also been reported for wet milled ogi and for yellow dent corn by Samapundo *et al*. (2007).

The result for 20CMN and 20CMQ (Figure 3) showed that EMC increases with $a_w$ at room temperature. Also, amount of water absorbed which is directly proportional to EMC increased with increased water activity. Sample 20CMQ absorbed more moisture than sample 20CMN at low water activity (between 0.1- 0.5). Johnson (2010) reported a similar trend between $a_w$ 0.05 and 0.4 for cassava flour and fermented maize meal. There could be several reasons for the observed trends. At $a_w$ 0.1 to 0.4 range, usually referred to as Zone

I, water molecules are mainly adsorbed onto hydrophilic', charged and polar groups of proteins and polysaccharides (Timmermann, 2001). The high tendency to absorb more moisture at lower $a_w$ for 20CMQ than the 20CMN may likely be implicated to higher protein content obtained for 20CMQ compare to the former.

Conversely, at $a_w$ above 0.5, very close to Zone 3 (i.e., a > 0.7), where water molecules are mechanically entrapped in the voids, crevices and capillaries, sample 20CMN was observed to absorbed more moisture than 20CMQ (Figure 3). The same thing was observed for plantain flour by Johnson (2010). This observation may be related to the fact that more starch molecules are hydrolyzed to sugar in 20CMN than 20CMQ (Chen & Lin. (2002). This implied that at high relative humidity (60-80%), 20CMN will deteriorate faster than 20CMQ as EMC have an important practical bearing on chemical and microbiological reactions associated with spoilage, hence, may affect the shelf life of food products as well (Shindano, 2007). The adsorption isotherm pattern obtained at room temperature for both samples are comparable to the result reported by Wicklow *et al*. (1998) in a hybrid maize grain, particularly at $25^0$C (corn flour ) and Abdullah *et al*. (2000) in their determination in corn flour (corn meal).

*BET Monolayer Moisture Content (Mo)*

This moisture content corresponds fairly well with the monolayer value, as determined from the BET isotherm equation or GAB isotherm equation. This monolayer value can be viewed as a critical moisture content which is associated with a critical Aw value (Bell and Labuza, 2000). The BET-monolayer estimation is an effective method for estimating the amount of water molecules bound to specific polar sites in a food matrix and it does not simply apply to the product surface. Incidentally, the estimated BET monolayer for 20CMN (3.43) is lower than 3.52 obtained for 20CMQ from the data on Table 1 and Figure 2. These values are close to the estimated monolayer moisture contents *gm M* by the GAB model from the adsorption isotherms for non-defatted white maize meal; 5.06 and 4.64 g/100 g db whereas for defatted white maize meal were 6.05 and 4.61 g/100 g db at 30 and $45^0$C, respectively (Shindano, 2007). Also, the value agrees with literature data for other starchy products, Chuzel and Zakhia, (1991), for “gari”, Kuye and Sanni, (2002) for “laun”, Sanni *et al*. (1997) for “fufu” and tapioca. A food product is most stable at its ‘‘monolayer moisture” content, which varies with the chemical composition, structure and environmental conditions, such as temperature.

## Conclusion

The adsorption isotherm result is a pointer that there is higher composition of starch and protein in co-milled normal endosperm and QPM flour, respectively. This is a contributing factor to either the stability or deteriorating tendency of dried flour product at room temperature. Also, BET monolayer moisture content which is an indication of stability was higher for QPM than for normal endosperm maize flour. Therefore, it can be concluded that at high relative humidity, flour from normal endosperm maize will deteriorate faster than that of QPM flour, meaning that the shelf-life of QPM flour will be longer than that made from normal endosperm.

## Recommendations

This study recommends that;

- To prolong the shelf-life of normal maize endosperm, it should be packaged in air- tight containers.
- Further studies on effect of packaging on the shelf –life of co-milled ogi flour are also advised.

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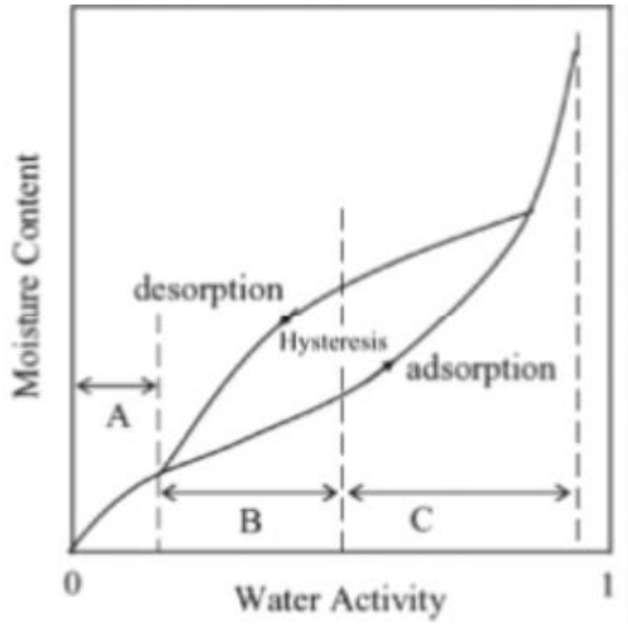


**Figure 1.** Sorption isotherm for a typical food product, showing the hysteresis

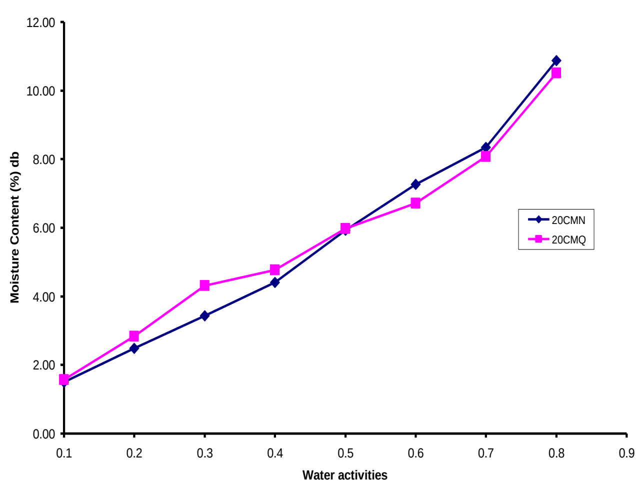


**Figure 2:** Adsorption isotherms of co-milled samples at room temperature (30±2 $^{o}$C)

**Key:** 20CMN- 20% carrot co-milled with normal maize, 20CMQ- 20% carrot co-milled with quality protein maize

**Table 1.** Experimental data for adsorption and monolayer plot of co-milled samples at room temperature (BET Model)

| **Samples** | **20CMN** | | **20CMQ** | |
|---|---|---|---|---|
| **Water activities** | **EMC (%) db** | $\frac{a_w}{(1-a_w)\,MC}$ | **EMC (%) db** | $\frac{a_w}{(1-a_w)\,MC}$ |
| 0.1 | 1.50±0.08 | 0.074 | 1.57±0.12 | 0.071 |
| 0.2 | 2.48±0.15 | 0.101 | 2.84±0.46 | 0.088 |
| 0.3 | 3.44±0.02 | 0.125 | 4.32±0.16 | 0.102 |
| 0.4 | 4.40±0.07 | 0.151 | 4.77±0.14 | 0.140 |
| 0.5 | 5.93±0.13 | 0.169 | 5.98±0.41 | 0.167 |
| 0.6 | 7.27±0.12 | 0.206 | 6.72±0.08 | 0.223 |
| 0.7 | 8.34±0.07 | 0.280 | 8.07±0.23 | 0.289 |
| 0.8 | 10.87±0.04 | 0.368 | 10.52±0.12 | 0.380 |

**Key:** 20CMN- 20% carrot co-milled with normal maize, 20CMQ- 20% carrot co-milled with quality protein maize