# Effect of Temperature on the Water Adsorption Isotherms of High-Pressure-Processing Barley Flour

**A thesis presented**

**By**

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## Content

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## Introduction

### Research Background:

Barley, one of the first cultivated grains in the world, is a major cereal grain grown in temperate climates globally. It has been widely considered that barley was widely grown in Eurasia in 10000 years ago. The exact origin of barley is actually debatable, possibly originating Egypt, Ethiopia, the near East or Tibet (1). Although barley is one of the earliest cultivated crops, its cultivation in China and India is thought to be occurred later. In 2005, barley was ranked fourth among grains in quantity produced, only behind maize, rice and wheat (2).

Barley is a member of grass family, which has many different varieties. From Genus *Hordeum L*, barley is from Monocot group, Poaceae Family. One way to classify barley is to identify it by whether there are two, four or six rows of grains on the head (3, 4, 5). Two-row barley can produce 25-30 grains, while six-row can produce 25-60 grains (6) (Figure 1.1). Two-row barley has a lower protein content than six-row barley while has a more fermentable sugar content. High-protein barley is suitable for animal feed. Low-protein barley is always used for malting because it needs shorter steeping and has less protein in the extract that can make beer cloudy. Six-row barley is common in American lager-style beers, when adjuncts such as corn and rice are used. In the meantime, two-row barley is popular in traditional German beers. Few research has been done on differentiating four-row barley because it has been believed that it is actually a loose six-row barley. Another way to classify barley is to describe the beards covering the kernels. In the barley germplasm database, beards (awned) are described along the following morphology (6).

1. Long awned
2. Short awned
3. Normal hooded
4. Elevated hooded
5. Subjacent hooded
6. Long awned in central row, and awnletted or awnless in lateral rows
7. Short awned in central row, and awnletted or awnless in lateral rows
8. Awnless or awnletted in central and lateral rows
9. Elevated hoods in central row, and awnless in lateral rows.

Barley can also be described as (7, 8, 9)

1. Hulled or hulless (naked)
2. Feed or malt type
3. Height (dwarf)
4. Seed color (colorless, white, yellow, blue)

(Research has shown that some hulless cultivars are resulting in more digestible, high-protein feed, especially for swine and poultry (10))


Figure 1.1 Two-Row and Six-Row Barley

Being known as a self-pollinating, diploid species with 14 chromosones (11), barley's wild ancestor, *Hordeum vulgare* subsp. *Spontanuem*, is abundant in grasslands and woodlands throughout the Fertile Crescent area of Western Asia and northeast Africa, and is abundant in disturbed habitats, roadsides and orchards.

In 2016/2017 crop year, barley production amounted to approximately 148.03 million metric tons. In 2017/2018 crop year, barley production is estimated to be 137.47 million metric tons, which represents a decrease of 9.57 million metric tons or a -6.51% in barley production globally (12). Below (Figure 1.2) is the graph of major barley producers in 2016/2017 crop year. As it is indicated from the graph, European Union produced the largest amount of barley, which is 59.9 million metric tons. It can

be also understood that barley has a wider ecological range than any other cereal because it is more adaptable than other cereals, tolerating many diverse environments except for acidic and wet soils. Barley can be grown on soils unsuitable for wheat, and at altitudes unsuitable for wheat or oats (13). Because it is highly tolerate with salty and dry environment, making it an attractive trait and it can be grown near dessert areas.

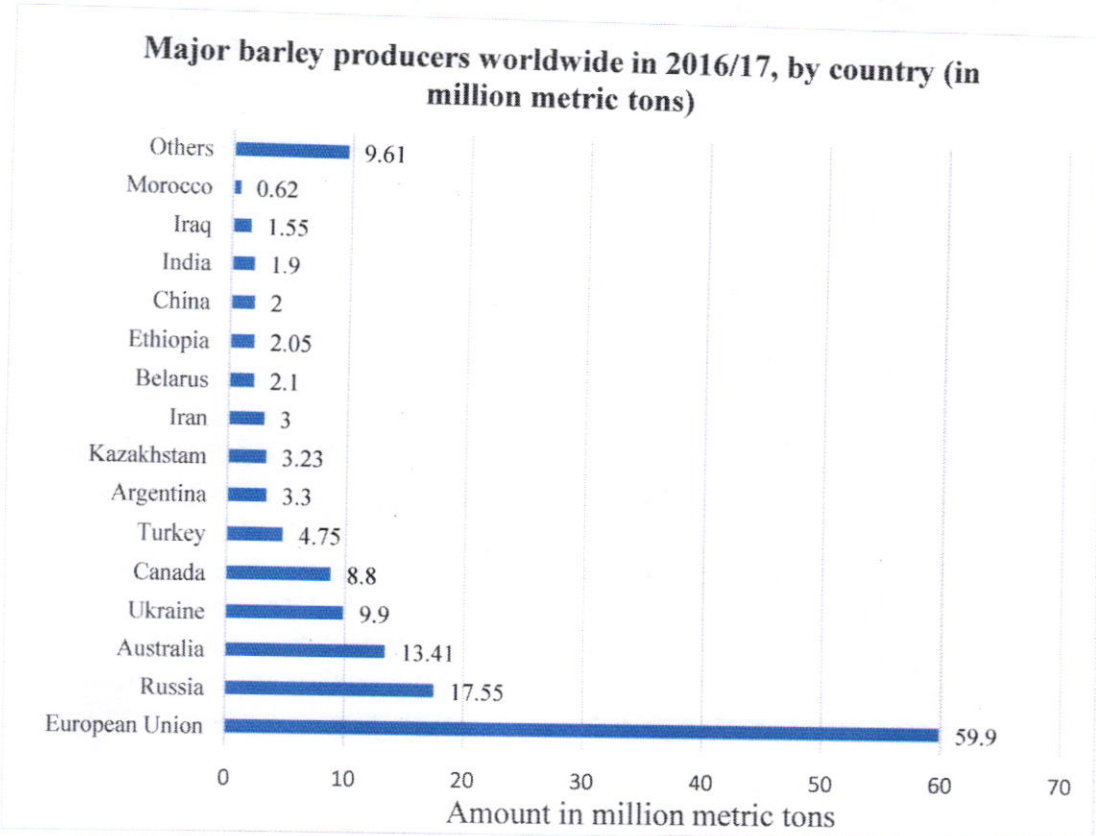


Figure 1.2 Major barley producers worldwide in 2016/2017, by country

Barley can be used in many different ways, however, the majority of all barley is used for animal feed consumption, or malting. High protein barleys are generally valued for food and feeding, and starchy barley for malting. Malting is one of the most important use of barley, which malt is used to produce beer distilled alcohol, malt syrup, malted milk, flavorings and breakfast foods. Both six-row and two-row barley varieties can be used for malting, but six-row varieties are ideal for beer (14). What is malting? Malting can also be defined as controlled sprouting, which is a complex interaction of genes involved in germination, growth and development (15). The reason why it is necessary to apply malting is that the starch, protein and nucleic acid molecules that are stored in barley grains. These large molecules are not good nutrients for brewing yeast or they are not good for supporting fermentation reactions performed by brewing yeasts.

For brewing yeasts to make good use of these nutrients, these large and structurally complex compounds must be partially degraded into sugars, amino acids and nucleotides. When barley seeds germinate, hydrolytic enzymes are synthesized or converted to active forms that can readily degrade these large compounds. Steps of malting include steep, germination, kilning, browning and optional bleaching. Steep is to raise moisture to 42-44% uniformly through kernel. The time for steep should not be too long or too short. If steep is too long, it could result in mold and bacteria grow; if steep is too short, poor malt will be formed. Germination is to put barley on beds with forced air and 100% RH 15 °C temperature. The purpose of this step is to release alpha-, beta-, amylase, glucosidase, dextrinase. These enzymes are temperature stable during drying. Kilning is to reduce moisture and dry malt, while browning to add flavor and color. After that, optional bleaching is applied to reduce some of the color. During malting, the acrospire (the plant shoot) grows along one side of the kernel. As it grows, pre-existing enzymes are released and new enzymes are created in the aleurone layer which "modify" the endosperm (the protein/carbohydrate matrix starch reserve) for the acrospire's use (16). Malted barley is the source of the sugars, primarily maltose, which are fermented into beer. The grain partially germinates, releasing enzymes in the aleurone layer (outermost layer of the endosperm). New enzymes are created that break down the endosperm's protein/carbohydrate matrix into smaller carbohydrates, amino acids and lipids, and open up the seed's starch reserves. The endosperm is composed of large and small starch granules that are packed in a protein matrix. The cell walls within the matrix holding the starch granules are primarily composed of beta-glucans (a type of cellulose), some pentosans (gummy polysaccharide) and some protein. The degree to which the enzymes unpack the starch granules (i.e. breakdown the endosperm) for use by the growing plant (or brewers) is referred to as the "modification." It refers to all of the polymer-degrading processes that occur during malting. One visual indicator that a maltster uses to judge the degree of modification is the length of the acrospire which grows underneath the husk. The length of the acrospire in a fully modified malt will typically be 75-100% of the seed length. Drying is used to stop the malting process when the proper balance between resources converted by the acrospire and resources consumed by the acrospire has been achieved (17). The reason of malting is to generate new these enzymes, to break down the matrix surrounding starch granules, prepare the starches for conversion, and then stop the reaction until the brewer is ready to utilize the grain. Finally, the green malt is dried with heat and the acrospire and rootlets are

knocked off by tumbling. The kiln drying of the new malt denatures many of the enzymes, but several types remain, including the ones necessary for starch conversion. The amount of enzymatic starch conversion potential that a malt has is referred to as its "diastatic power" (17). Figure 1.3 indicates the change of barley kernel during malting.

Figure 1.3 Change of Kernel during Malting

Beta-glucans are soluble dietary fiber component of barley and oat bran. It is important for the malting industry and indicates how well the endosperm is modified (16). High levels of beta-glucan can cause a viscous wort that may cause problems with filtration or hazy beer. Thus, lower levels of beta-glucan are preferred for brewing.

Brewing is the production of beer by steeping barley malts in hot water and fermenting the resulting sweet liquid with yeast. During brewing, malted barley is soaked in hot water to release the malt sugars. Then the sugar solution is boiled with hops for seasoning. After seasoning, the solution is cooled and yeast is added to start fermentation. During the fermentation, sugars are digested, and $CO_2$ and ethyl alcohol is produced. When the fermentation is completed, the beer is bottled and added with sugar to provide the carbonation (17). A high quality malt will contain the right amount of hydrolytic enzymes and metabolites to fulfill these requirements and will have the right degree of friability to allow many of its components to be readily solubilized during mashing (18). During malting and mashing, the barley starch should be almost completely degraded into sugars that can be utilized by the brewing yeasts, whereas

only about 45% of the barley protein should be solubilized. Too much protein solubilization is thought to result in beers with poor foaming characteristics (18). When insufficient protein hydrolysis occurs, the remaining proteins may interact with polyphenols to form beer haze precipitates

Four amylolytic enzymes are generally thought to participate in converting the starch in malted barley into fermentable sugars: these are a-amylase, b-amylase, a-glucosidase and limit dextrinase. During brewing, amylase enzymes digest amylose (linear starch) and amylopectin (branched starches) into hexose sugars (19). The sugars are a nutrient source for the yeast to facilitate fermentation. Sufficient sugars are needed to obtain the desired alcohol level.

In addition to malting, another important use of barley is for animal feed and human consumption. As nutritional scientists claimed that barley is a very good source of molybdenum, manganese, dietary fiber, and selenium, and a good source of copper, vitamin B1, chromium, phosphorus, magnesium, and niacin (20). Barley can provide bulk and decrease transit time of fecal matter, thus decreasing the risk of colon cancer and hemorrhoids, barley's dietary fiber also provides food for the "friendly" bacteria in the large intestine. As those Eco-friendly bacteria ferment barley's insoluble fiber, they produce a short-chain fatty acid called butyric acid, which serves as the primary fuel for the cells of the large intestine and helps maintain a healthy colon. These helpful bacteria also create two other short-chain fatty acids, propionic and acetic acid, which are used as fuel by the cells of the liver and muscles (20). Propionic acid is proved to have effect on lowering cholesterol. In an animal studies, propionic acid has been shown to inhibit *HMG-CoA reductase*, an enzyme involved in the production of cholesterol by the liver (21). By lowering the activity of *HMG-CoA reductase,* propionic acid contributes to lowering blood cholesterol levels.

Besides, barley's dietary fiber is high in beta glucan (Figure 1.4), which helps to lower cholesterol by binding to bile acids and removing them from the body via the feces. Bile acids are compounds used to digest fat that are manufactured by the liver from cholesterol (22). When they are excreted along with barley's fiber, the liver must manufacture new bile acids and uses up more cholesterol, thus lowering the amount of cholesterol in circulation. Soluble fiber may also reduce the amount of cholesterol manufactured by the liver. As it is published in the *American Journal of Clinical*

*Nutrition*, barley's fiber has multiple beneficial effects on cholesterol. In this study of 25 individuals with high cholesterol (postmenopausal women, premenopausal women, and men), adding barley to the American Heart Association Step 1 diet resulted in a significant lowering in total cholesterol in all subjects, plus their amount of large LDL and large and intermediate HDL fractions (which are considered less atherogenic) increased, and the smaller LDL and VLDL cholesterol (the most dangerous fractions) greatly decreased (23). In most cases, beta-glucans form a linear backbone with 1,3 beta-glycosidic bonds but vary with respect to molecular mass, solubility, viscosity, branching structure, and gelation properties, causing diverse physiological effects in humans and animals. Barley grain usually contains 2-10% beta-glucan (24). Waxy starch phenotypes are usually associated with high beta-glucan content, waxy endosperm types generally have greater beta-glucan contents than barley types with normal starch (25). Although beta-glucans are considered to be problems in beer brewing, causing a viscous wort that may cause problems with filtration or hazy beer, high level of beta-glucans are beneficial to human health.

Barley's fiber can prevent or help with a number of different conditions. A study confirmed that eating high fiber foods, such as barley, helps prevent heart disease. Almost 10,000 American adults participated in this study and were followed for 19 years. People eating the most fiber, 21 grams per day, had 12% less coronary heart disease (CHD) and 11% less cardiovascular disease (CVD) compared to those eating the least, 5 grams daily. Those eating the most water-soluble dietary fiber fared even better with a 15% reduction in risk of CHD and a 10% risk reduction in CVD (26). The

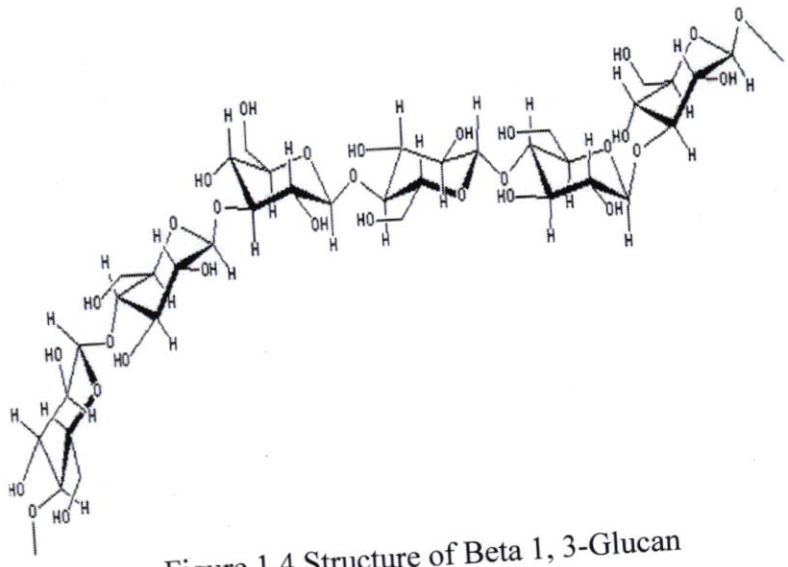

Figure 1.4 Structure of Beta 1, 3-Glucan

fiber in barley can also help to prevent blood sugar levels from rising too high in people with diabetes. FDA suggests that people should increase their intake of barley not only for the benefits of lowering the cholesterol level but also for the potential of reducing the risks of having heart diseases. Barley is a good source of niacin, which is a vitamin B that provide numerous protective actions against cardiovascular risk factors。 Niacin has an effect on reducing total cholesterol and *lipoprotein (a)* levels. *Lipoprotein (a)* is a molecule composed of protein and fat that is found in blood plasma and is very similar to LDL cholesterol, however, it is even more dangerous as it has an additional molecule of adhesive protein named *apolioprotein (a)*, which renders *Lipoprotein (a)* more capable of attaching to blood vessel walls (26). Niacin may also help prevent free radicals from oxidizing LDL, which only becomes potentially harmful to blood vessel walls after oxidation. Lastly, niacin can help reduce platelet aggregation, the clumping together of platelets that can result in the formation of blood clots. One cup of barley soup will supply you with 14.2% of the daily value for niacin.

Beta-glucans in barley not only have benefits on reduction of blood cholesterol and glucose and weight loss by increased satiety, but also have functional properties in food-processing and end-use quality, with the exception of beer brewing as it was mentioned in the above text. Positive relationships between beta-glucan content and water uptake during cooking and the crumb moisture content of bread baked with 30% barley flour, and a negative relationship with the hardness of cooked noodles containing 30% barley flour were reported (27). Molecular structure of cereal beta-glucans and physical and functional properties of isolated oat and barley beta-glucans incorporated into various food products are also mentioned by scientists in 2007 (28).

Although barley has been proved to have plenty of health benefits, there are huge difficulties on commercial processing of barley food products due to its high viscosity. The amylose content of barley starch varies from 0% in zero amylose waxy to 5% in waxy, 20-30% in normal and up to 45% in high-amylose barley (29). Barley exhibits lower pasting temperature, and greater hot-paste viscosity, swelling power, granule fragility and freeze-thaw stability. People can both direct intake barley and intake barley-product indirectly. In Asia countries, wheat and rice are the major staple in people's dining tables, while barley is not that common as staple diets. As human's eating habits took a long time to get changed and developed, it is not that reasonable to change Asian's dietary structure. Another way is to manufacture barley functional food

products, such as barley soup or different types of products. However, the viscosity of barley-water mixture is much higher than other starch with water, making it extremely difficult in food processing. Therefore, lowering viscosity of barley has been studied by many scholars.

**Previous Research**

Previous research has indicated that barley flour treated under 600 MPa has a relatively lower viscosity than normal barley flour (30). High-pressure-processed barley flour was added with water for the barley starch to gelatinize. The temperature was adjusted for starch to fully be gelatinized. After the treated barley flour samples were fully become gelatinization, the viscosity was continuously measured by Rapid Viscosity Analyzer. As gelatinization starts, the viscosity first reaches to the highest amount. After 10 minutes, the viscosity reaches to the lowest amount. Then the viscosity starts to increase again and then remain in a constant number, which is named as final viscosity. In this research, the change of viscosity of pressure-treated barley flour followed the trend of gelatinization of normal starch (Figure1.5). However, barley flour treated under 550 MPa and 600 Mpa had relatively lower amount of the highest viscosity and final viscosity than barley flour without pressure treatment. The highest viscosity during gelatinization decreased as the pressure treated on barley flour increased (Figure 1.6). As it was indicated in the research, the highest viscosity of untreated barley flour during gelatinization was 5400 cP.The highest viscosity of barley flour continued to tank as the treated pressure increased but not larger than 300 MPa. During 350 MPa to 450 MPa, the highest viscosity increased. Barley flour treated under 550 MPa had much lower amount of the highest viscosity in gelatinization. The highest viscosity in gelatinization of barley flour treated under 600 MPa was 2700 cP.

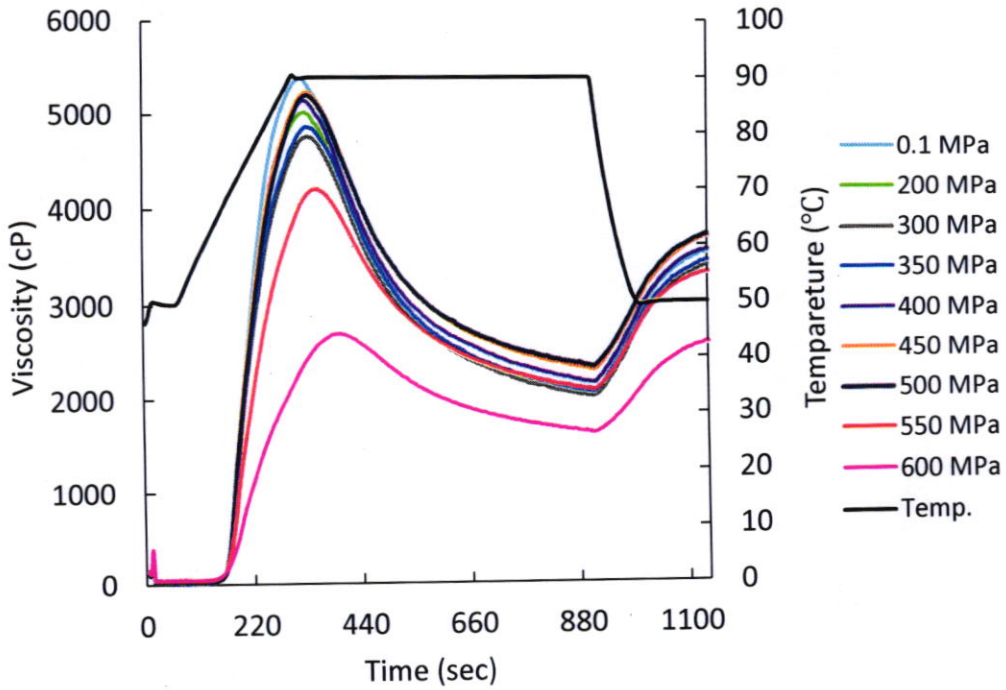


Figure 1.5 Gelatinization of High-Pressure-Processed Barley (47)

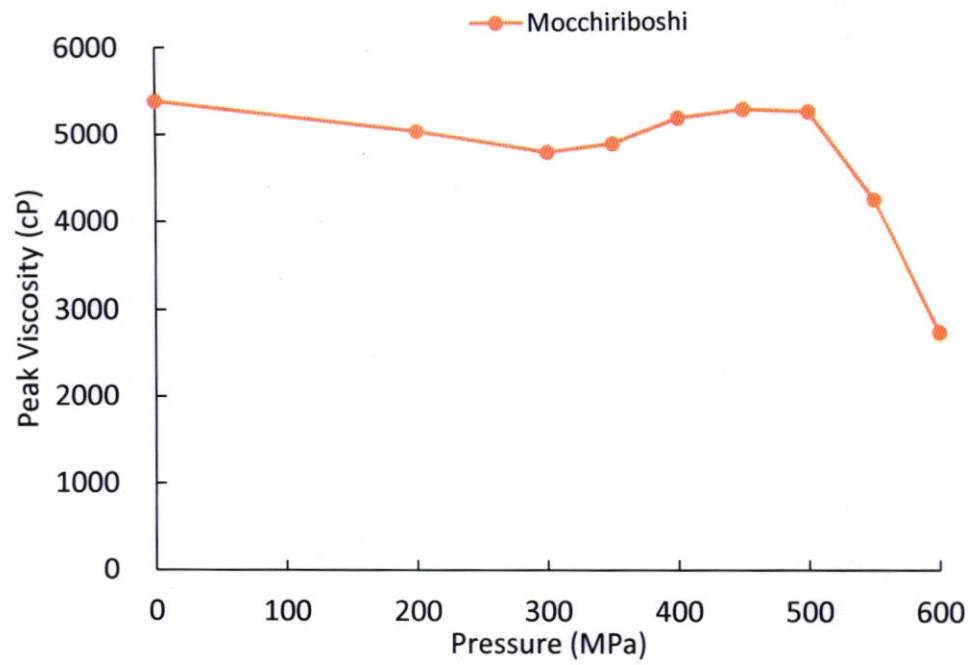


Figure 1.6 Relation between Highest Viscosity and Pressure (47)

The reason accounting for the decrease of viscosity after high pressure processing was also been studied. Treated with high pressure, the damaged starch rate increased, indicating high pressure caused damage in starch granules. It was also been

proved that swelling power decreased as treated pressure increased. According to X-ray diffraction (Figure 1.7), the type of crystals of barley flour granules is a combination of type V and type B. In 20° , a new peak can be observed. Based on all these evidence, it was been estimated that amylose-lipid complex was formed during high pressure processing (31). The formation of amylose-lipid complex is assumed to have close relation with the decrease of viscosity. Amylose-lipid complex could increase the solving temperature of amylose, making it more difficult for amylose in starch to get dissolved in water. In order to get dissolved, one has to reach to higher temperature. Amylose-lipid complex is capable of inhibiting moisture absorption of starch granules. Last but not least, amylose-lipid complex combines with amylose in starch granules, reducing the amount of free amylose. As the amount of free amylose decreases, fewer amylose dissolved in water, resulting in inhibiting the elevation of viscosity.

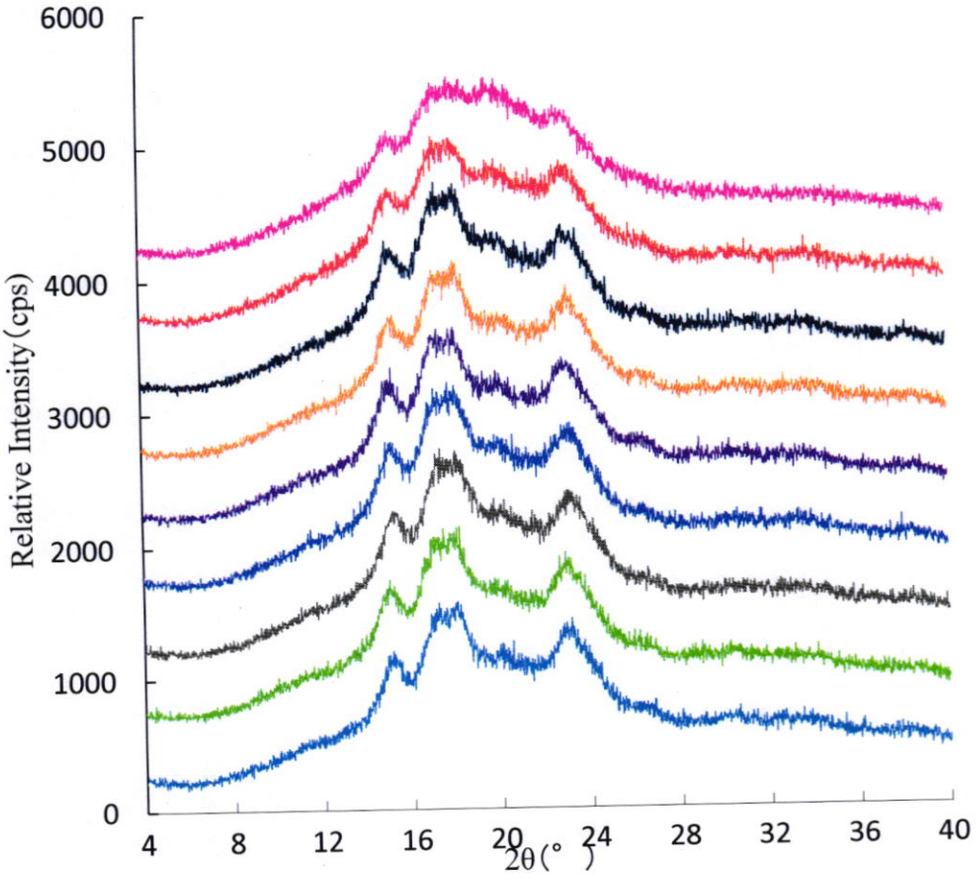


Figure 1.7 X-ray Barley Flour (47)

**oisture Absorption Isotherm**

Moisture sorption isotherms describe the relationship between moisture content d water activity in food. The water contained in food appears in different forms based ı the interactions that exist between the components of food and water molecules (32). he concept of water activity ($a_w$) comes from a series of thermodynamic onsiderations that entail the chemical potential mathematical expression of the omponent, which constitutes the tendency of a component to escape the system. It can also be defined as the ratio of water vapor pressure at a constant value of pressure and temperature. Another widely-accpeted definition is the equilibrium relative humidity of the air surrounding the food at the same temperature (33), and it can be expressed in equation1.

$$a_{w,f} = a_{w,v} = \frac{p_v}{p_{v,sat}} \qquad \textbf{Equation 1.}$$

Where f: food; v: vapor; v,sat: pure water vapor pressure.

Water activity of food equals the relative humidity of the air above it divided by 100, indicating that an equilibrium has been reached, constituting a form of measurement of the water amount available in food for a reaction series of biochemical and microbiological nature (33-35).

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. It is important to understand sorption isotherms in food science and technology because of design and optimization of drying equipment, design of packages, predictions of quality stability, shelf-life and calculation of moisture changes that may occur during storage. Several preservation processes were developed for the purpose of extend the shelf-life of food products in the way of lowering the availability of water to microorganisms and inhibiting enzymatic reactions (32, 36-40). 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. Water activity depends on the composition, temperature and physical state of the compounds (41).

How to acquire sorption isotherms. Empirically, sorption isotherms can be generated from an adsorption process or a desorption process; the difference between the curves is defined as hysteresis (Figure 1.8). Water adsorption by food products is a process in which water molecules progressive and reversibly mix together with food solids via chemisorption, physical adsorption, and multilayer condensation. One 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 adsorbed by hydrophilic and polar groups of food components (polysaccharides, proteins and so on). 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 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 t those of the free water that is held in voids, large capillaries, crevices; and the water in this region loosely binds to food materials (42-45). 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 favorable 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 molecule shrinkage theory, the capillary condensation, and the swelling fatigue theory (46).

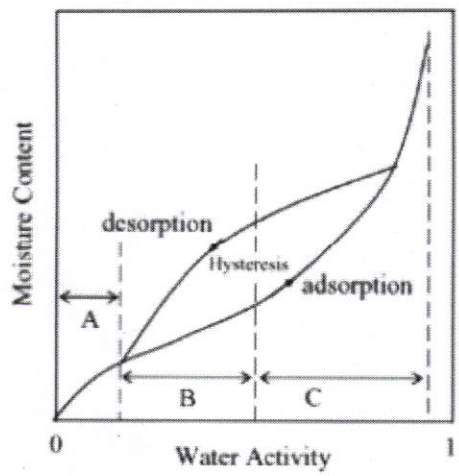


Figure 1.8 Sorption Isotherm for a Typical Food Product, showing the hysteresis

Brunauer et al., 1940 (47) classified sorption isotherms according to their shape and processes, establishing five different types; as it is shown in Figure 1.9. Type 1: Langmuir and/or similar isotherms that present a characteristic increase in water activity related to the increasing moisture content; the first derivative of this plot increases with moisture content and the curves are convex upwards. This type of sorption isotherm is typically applicable in the process of filling the water monomolecular layer at the internal surface of a material. Type 2: sigmoidal sorption isotherms, in which the curves are concave upwards; it takes into account the existence of multilayers at the internal surface of a material. Type 3: known as the Flory-Huggins isotherm, it accounts for a solvent or plasticizer such as glycerol above the glass transition temperature. Type 4: it describes the adsorption of a swellable hydrophilic solid until a maximum of site hydration is reached. Type 5: the Brunauer-Emmett-Teller (BET) multilayer adsorption of water vapor on charcoal and it is related to the isotherms type 2 and type 3. The two isotherms most frequently found in food products are the types 2 and 4 (48-50).

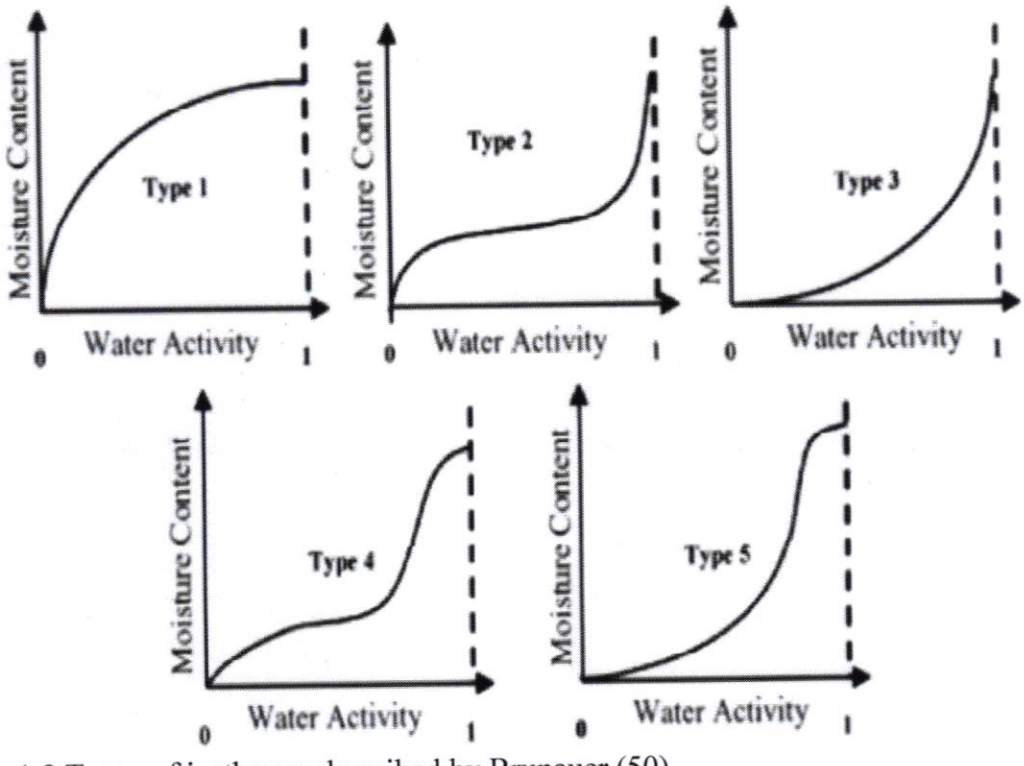


Figure 1.9 Types of isotherms described by Brunauer (50)

In order to mathematically express the relation between the water activity of food and its moisture content, diverse models have been developed such as nonlinear, linear, regressional models, constituted in their parameters by two, three, four, and six partial regression coefficients, which explain each one of the three zones that the isotherm of sorption of humidity conforms. In many cases, the model that is suitable for certain food product is not suitable for a different one, what is more, the model only exhibits a suitable predictive ability for certain moisture activity ranges.

Several mathematical models have been proposed to describe sorption isotherms. Some of them were developed with theoretical basis to describe adsorption mechanisms (35, 43); whereas the others are just empirical or a simplification of more elaborate models. In some ranges of water activity, sorption isotherms can be approximated to linear equations (44). There are some semi-empirical equations with two or three fitting parameters to describe moisture sorption isotherms. The most common equations that are used for describing sorption in food products are the Langmuir equation, the BET equation, the Oswin model, the Smith model, the Iglesia-Chirife equation, the GAB model, and the Peleg model (22).

**Langmuir equation**

Langmuir proposed the following physical adsorption model on the basis of unimolecular layers with identical and independent sorption sites, and which is expressed as it is shown in equation 2:

$$a_w \left(\frac{1}{M_w} - \frac{1}{M_0}\right) = \frac{1}{C\,M_0} \qquad \textbf{Equation 2.}$$

where Mw is the equilibrium moisture content(kg water/kg dry matter), M0 is the monolayer sorbate content (kg water/kg dry matter) and C is a constant.

The value of the monolayer (M0) is of particular importance because it indicates the amount of water that is strongly adsorbed in specific sites, and it is considered to be the value at which a food product is the most stable. Langmuir's isotherm is the most crucial equation among the theoretical models, which is based on the forces acting between the product surface and the water condensed from the vapor as a

monomolecular layer. The extensions of the Langmuir's underpinning idea on multi-molecular layers result in the BET and GAB isotherms, which are able to describe sigmoidal shaped isotherms commonly observed in the case of food and other materials of biological origin (45).

**Brunauer-Emmett-Teller (BET) equation**

The BET equation (equation 3), which is the most widely used model in food systems, was first proposed by Brunauer, Emmett and Teller (43). It represents a fundamental milestone in the interpretation of multi-layer sorption isotherms, particularly the types II and III. It is also an effective method for estimating the amount of bound water in specific polar sites of dehydrated food systems (22, 48).

$$M_w = \frac{M_0 C a_w}{(1-a_w)(1+(C-1)a_w)} \qquad \textbf{Equation 3}$$

where M 0 is the monolayer moisture content, which represents the moisture content at which the water attached to each polar and ionic groups starts to behave as a liquid-like phase. And, C is the energy constant related to the net heat of sorption; it is related to the difference between the molecules that sorb energy of the first layer and the other remaining layers. These constants are also the constant characteristic of the isotherm of sorption of monolayer of Langmuir. Almost in all cases, the deviation of the linearity of these graphs indicates that, at high vapor pressures, the amount adsorbed by the sorbent is lower than the one predicted by the isotherm (22, 49).

The BET equation represents a basis in the interpretation of isothermal sorption multilayers and it has been applied in gas adsorption and porous steam in surfaces and solids, as well as in water, especially in steam absorption, by homogenous polymers and other materials. Nevertheless, the considerable success of the isotherm is rather qualitative that quantitative. If we considered the linearized forms of the equations of isotherms as the estimation of the applicability rank that they own in its linear sections, it can be observed that, in almost all cases, BET graphs are linear only in a limited range of water activity from 0.05 to 0.45. This difficulty in the process of fitting the experimental dates on the totality of the range of relative pressure application

determined that the main application of the BET equation is the one related to the estimation of surface areas (49). The theory behind the development of the BET equation has been questioned due to the assumptions that (a) the rate of condensation on the first layer is equal to the rate of evaporation from the second layer; (b) the binding energy of all of the adsorbates on the first layer is same; and (c) the binding energy of the other layers is equal to the one of pure adsorbates. The assumptions of a uniform adsorbent surface and the absence of lateral interactions between adsorbed molecules are incorrect, considering the heterogeneous food surface interactions. Nevertheless, the theoretical basis that provided this isotherm stimulated the investigation for developing alternatives that broaden the scope of the BET equation, or for reformulating the model to find new physical approaches (38, 50). The BET equation can be considered to be the most useful for determining the optimum moisture conditions for good storage stability, especially for dehydrated food products (31). The parameters of the BET equation for different food products are listed on table 1.1.

**Table 1.1.** Estimated parameters of the BET equation for various food products.

| Product | Temp.°C | $M_0$ | C | $R^2$ | Type |
|---|---|---|---|---|---|
| Corn flour | 22 | 0.056 | 502.82 | 0.99 | A |
| Yam | 45 | 0.706 | 2.908 | 0.91 | D |
| Dried potato * | 30 | 0.078 | 7.345 | nr | D |
| Dried potato * | 30 | 0.055 | 9.226 | nr | A |
| Dried tomato | 30 | 0.1624 | 14.06 | nr | A |
| Apples ** | 30 | 0.137 | 26.430 | nr | A |
| Apples ** | 30 | 0.234 | 20.166 | nr | D |
| *Chhana podo* *** | 35 | 0.04834 | 4.464 | 0.994 | D |
| Blueberry | 40 | 0.067 | 5.743 | nr | A |
| Blueberry | 40 | 0.100 | 101.45 | nr | D |

nr: not reported; D: desorption; A: adsorption.

* $a_w$ range: 0.1–0.5; ** $a_w$ range: 0.11–0.5; *** $a_w$ range: 0.25–0.54.

**Oswin model**: It is an empirical model that consists in a series expansion for sigmoid shaped curves and it was developed by Oswin, 1946. Its equation is as below:

$$M_w = C\left(\frac{a_w}{1-a_w}\right)^n$$

Where C and n are constants.

The Oswin model was used to relate the moisture content of fatfree dry milk and freeze dried tea up to a water activity of 0.5, as well as for various food listed in Table 1.2.

Table 1.2. Estimated constants of the Oswin model for several food products

| Product | Temp. °C | C | n | $R^2$ |
|---|---|---|---|---|
| Corn flour | 22 | 0.106 | 0.299 | 0.99 |
| Yam | 45 | 0.353 | 0.495 | 0.991 |
| Dried potato | 30 | 0.125 | 0.461 | nr |
| Dried potato | 30 | 0.103 | 0.548 | nr |
| Dried tomato pulp | 30 | 0.303 | 0.441 | nr |
| Dried cashew apple | 30 | 10.72 | 0.581 | 0.9979 |
| Banana pulp | 20 | 0.164 | 1.122 | 0.9869 |
| Mango pulp | 20 | 0.114 | 0.855 | 0.992 |
| Garlic | 50 | 0.095 | 0.720 | 0.991 |
| Apple | 50 | 0.332 | 0.670 | 0.9786 |

**Halsey Model:** This model provides an expression for the condensation of multilayers at a relatively large distance from the surface, assuming that the potential energy of a molecule varies as the inverse power of its distance from the surface. This equation is good representation of the absorption data regarding isotherms type I, II and III. Moreover, this equation described the sorption behavior of food products that contain starch. This model is descried as it is expressed as below:

$$M_w = M_o\left(-\frac{A}{RT\ln a_w}\right)^{1/n}$$

Where A and n are constants; R is the universal gas constant; T is the absolute temperature; and $M_0$ is monolayer moisture content.

Since the use of the RT term does not eliminate the temperature dependence of A and n, the Halsey equation was modified by Iglesia and Chirife, 1976 into the following form, as it is described in the equation as below:

$$M_w = \left( - \frac{C}{\ln a_w} \right)^{1/n}$$

Where C and n are constants. The Halsey model was used for various food products, as it is listed in Table 1.3.

Table 1.3 Estimated Parameters of the Halsey Model for Various Food Products.

| Product | Temp. °C | C | n | $R^2$ |
|---|---|---|---|---|
| Corn flour | 22 | 0.002 | 2.516 | 0.96 |
| Pear osmotic dehydration | 40 | 0.178 | 0.666 | 0.99 |
| Pear | 40 | 0.147 | 0.853 | 0.99 |
| Banana pulp | 20 | 0.185 | 0.756 | 0.9871 |
| Blueberry | 40 | 0.108 | 0.890 | nr |
| Blueberry | 40 | 0.056 | 1.672 | nr |

Nr: not reported;

**Henderson model:** This is a commonly used model and it can be expressed as it is described in the equation listed below:

$$M_w = \left( - \frac{\ln(1 - a_w)}{C} \right)^{1/n}$$

Where C and n are constants.

According to this model, a plot of $\ln(-\ln(1-a_w))$ versus $\ln M_w$ should give as a result a straight line. However, Rockland observed three localized isotherms that did not provide precise information on the physical state of water. The constants of the Henderson model in different food products are listed on Table 1.4.

Table 1.4 Parameters of the Henderson Model for Various Food Products

| Product | Temp. °C | C | n | $R^2$ |
|---|---|---|---|---|
| Passion fruit peel | 25 | 2.160 | 0.591 | 0.990 |
| Pineapple peel | 25 | 2.04 | 0.601 | 0.993 |
| Yam | 45 | 0.126 | 0.126 | 0.933 |
| Dry cashew apple | 30 | 0.0509 | 1.08 | 0.9926 |
| Walnut kernels | 25 | 0.037 | 1.781 | 0.9854 |
| Walnut kernels | 25 | 0.123 | 1.267 | 0.9990 |

**Significance of Research**

As previous research indicated the potential of high pressure processing of lowering the viscosity of barley flour, it is possible for pressurized barley flour to be commercially manufactured into functional products. However, it is important to understand sorption isotherms of both barley flour and high pressure treated barley because of design and optimization of drying equipment, design of packages, predictions of quality stability, shelf-life and calculation of moisture changes that may occur during storage. Several preservation processes were developed for the purpose of extend the shelf-life of food products in the way of lowering the availability of water to microorganisms and inhibiting enzymatic reactions (32, 36-40). In this experiment, moisture absorption isotherms of barley flour samples (0 MPa, 200 MPa and 600 MPa) were measured and the experimental data was fitted with absorption isotherm model.

**Method:**

Barley Flour (Mocchiriboshi, 7.2% protein, 1.6% fat, 77.5% starch) used in this experiment were bought from Nagakura Company (Figure 2.1). The material was manufactured in 2014, which was also used in the experiment named *Effect of High Pressure Processing on Adjusting Viscosity of Barley Flour-Water Mixture*. The experiment was completed by previous member Mr. Sasao Shoji.

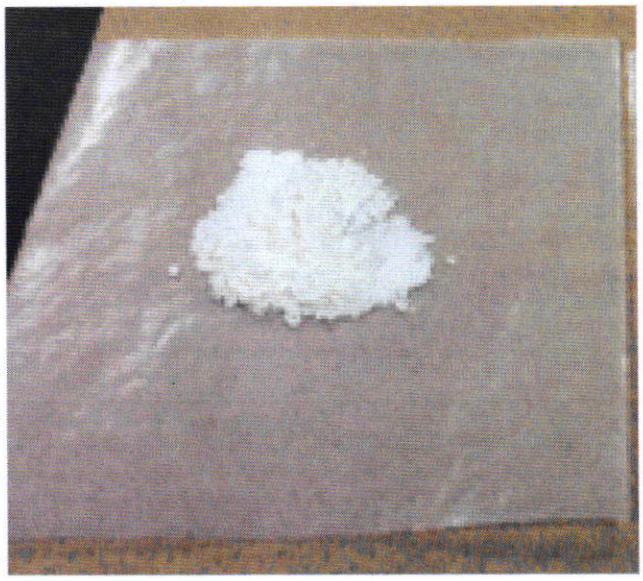

Figure 2.1 Appearance of Mocchiriboshi

Barley flour dough samples were prepared by adding 40 grams of flour with 40 grams of distilled water in one-300-mL-Beaker. A glass rod was used for mixing the flour with distilled water until barley flour dough was formed. Polyethylene bags (FLAEM NUOVA, MAGIC VAC roll, ACO-1025) were used pack barley flour dough and the samples were vacuum-sealed by vacuum sealer (TM-H) manufactured by FURUKAWA MFG. CO., LTD., which the air was deflated for 15 seconds and then the polyethylene bags were sealed for 2 seconds.

Barley flour dough samples were stored in one refrigerator under 4°C for two days. After two days, the samples were sent to Niigata University of Pharmacy and Applied Life Sciences to perform high pressure processing (The machine was shown in Figure 2.2). Vacuum-packaged Mocchiriboshi samples were pressurized under 200 MPa and 600 MPa through water pressure under 20°C. After the water pressure reached

to the set pressure, and the temperature reached 20°C, the samples were remained in the pressure for 10 minutes.

Figure 2.2 is the photo of the High Pressure Processing Machine that was applied in this experiment. High pressure processing can be generated either by direct compression (Figure 2.3 and Figure 2.4) and indirect compression("<The principles of ultra high pressure technology and its.pdf>,"). In this experiment, direct piston-type compression was applied to increase pressure. The pressure medium in the high pressure vessel is directly pressurized by a piston, driven at its larger diameter end by a low pressure pump.


Figure 2.2 High Pressure Processing Machine

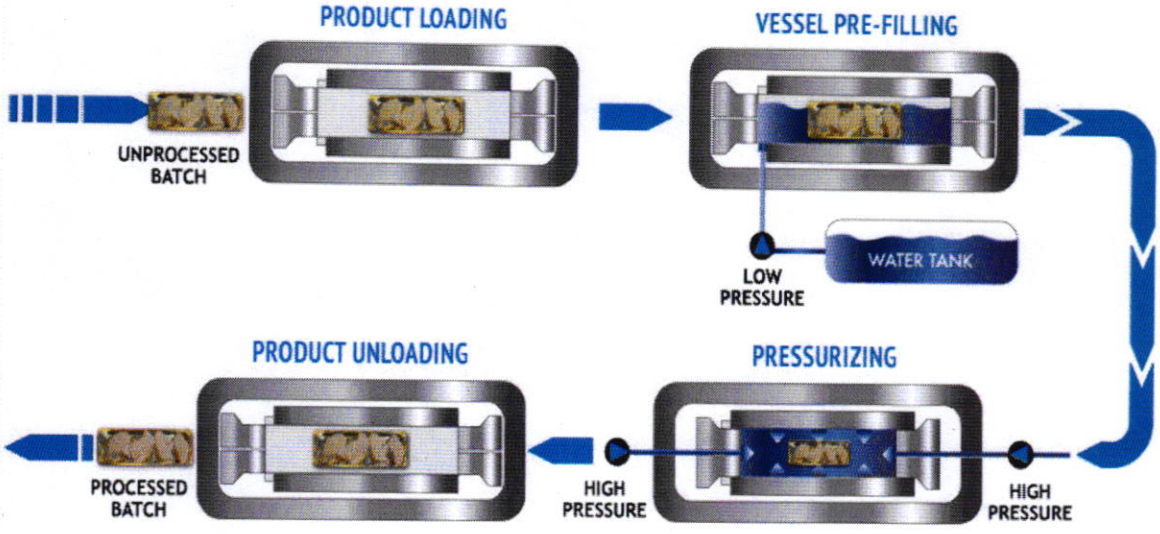


Figure 2.3 Principle of High Pressure Processing

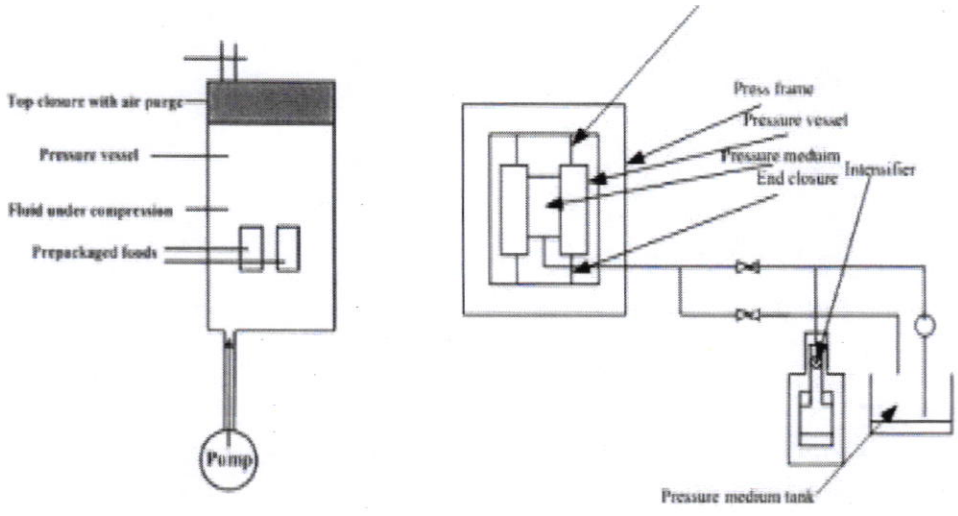


Figure 2.4 Direct method for generation of high isostatic pressure uses a piston driven by a high- pressure pump

The pressurized samples were stored in one freezer under -80°C for two days. After that, the freezing samples were divided into small pieces through using a hammer. The, the small samples were added in the beaker and performed freeze-drying for 24 hours. The air in the beaker was removed by using a pump (manufacture by EDWARD

Co., Ltd.) to reduce the pressure until -0.1 MPaG. The freeze-drying machine is shown in Figure 2.5. After freeze-drying, the samples were grounded into powder and ready for measurements.

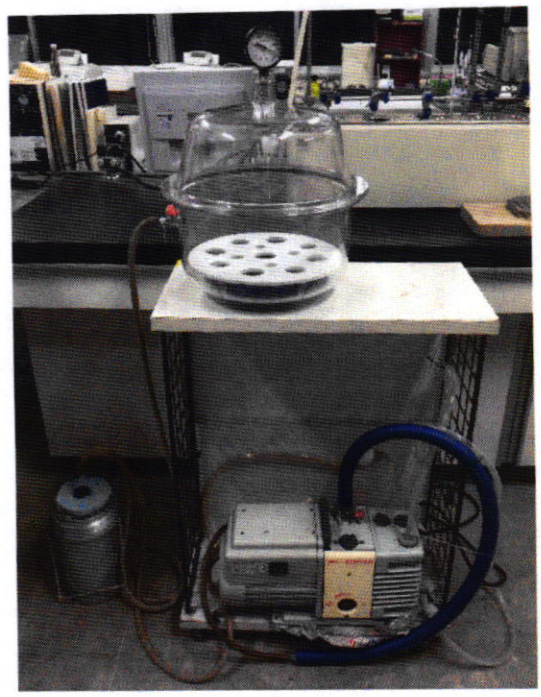

Figure 2.5 Freeze-Drying Machine

The equilibrium moisture contents of samples were determined by a gravimetric technique, in which the weight was weighed discontinuously within a thermally stabilized desiccators (Figure 2.6 and Figure 2.7). For absorption, a 2.000g sample of the freeze-dried pressurized mocchiriboshi flour was placed in a petri dish inside a desiccator. Each experiment was carried out in triplicate.

Saturated solutions with different water activities (Table 2.1) were used to maintain relatively humidity inside the desiccators. The desiccators were then placed in an incubator (Figure 2.7) under 20, 25, 30 and 35°C. The samples were weighed once every two hours until they reached equilibrium. The samples were equilibrated until there was no significant weight change, as evidenced by constant weight values ($\pm 0.001g$). The period for the barley flour dough to reach equilibrium is 48 hours. The experiment was carried out in triplicate.

Figure 2.6 the Image of Desiccators

Figure 2.7 the Image of Incubator

Table 2.1 Water Activity of Various Saturated Solutions in the Experiment

| Saturated Solutions | Water Activity |
|---|---|
| Lithium chloride | 0.07 |
| Potassium acetate | 0.11 |
| Magnesium chloride hexahydrate | 0.224 |
| Lithium nitrate | 0.33 |
| Sodium bromide | 0.47 |
| Potassium nitrate | 0.577 |
| Sodium hydroxide | 0.752 |
| Sodium chloride | 0.924 |

**Results:**

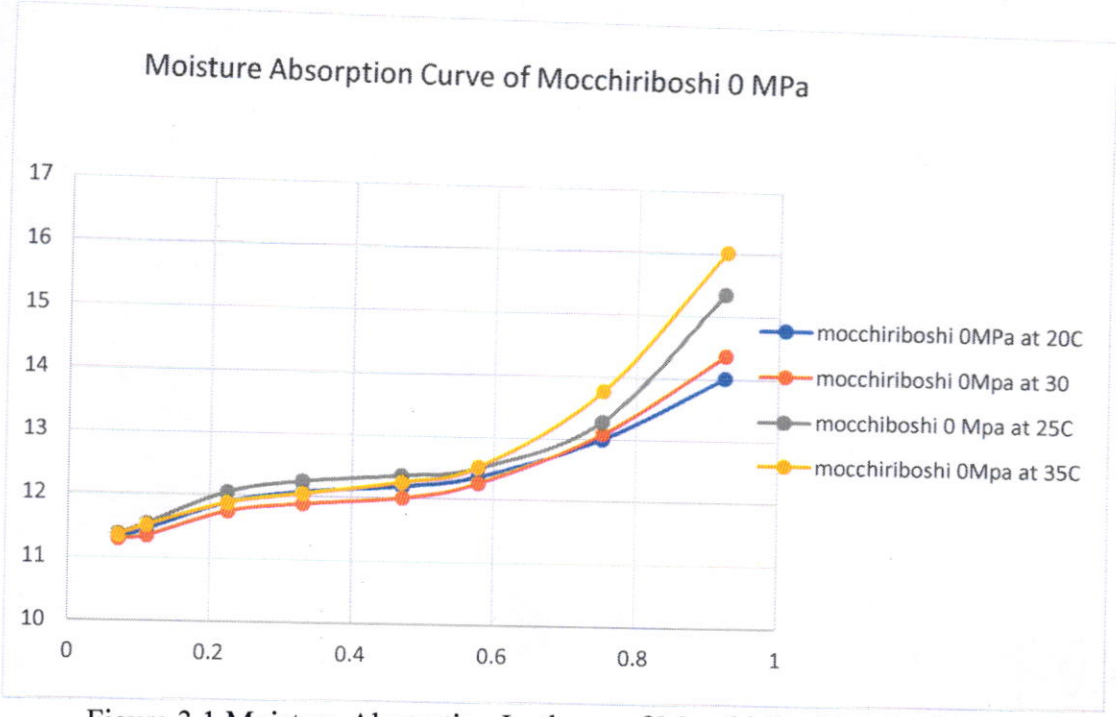


Figure 3.1 Moisture Absorption Isotherm of Mocchiriboshi under 0 MPa

As it is indicated in Figure 3.1, moisture absorption isotherms follows type 2 isotherms in all temperature. However, the moisture content is varied in mocchiriboshi being treated under different temperature. The moisture content of the samples firstly increased quickly as the water activity became higher. However, the speed of increasing moisture content became stable from 0.4 to 0.6. When water activity was over 0.6, moisture content increased largely. The moisture absorption isotherms of barley flour with no high pressure processing treatment followed strictly with sigmoidal shape as introduced in the above text. However, the moisture content differed as the incubation temperature changes. In the beginning, the moisture content was higher in barley samples with lower incubation temperature. After water activity was over 0.5, the moisture content of barley samples with higher incubation temperature tent to reach to higher amount.

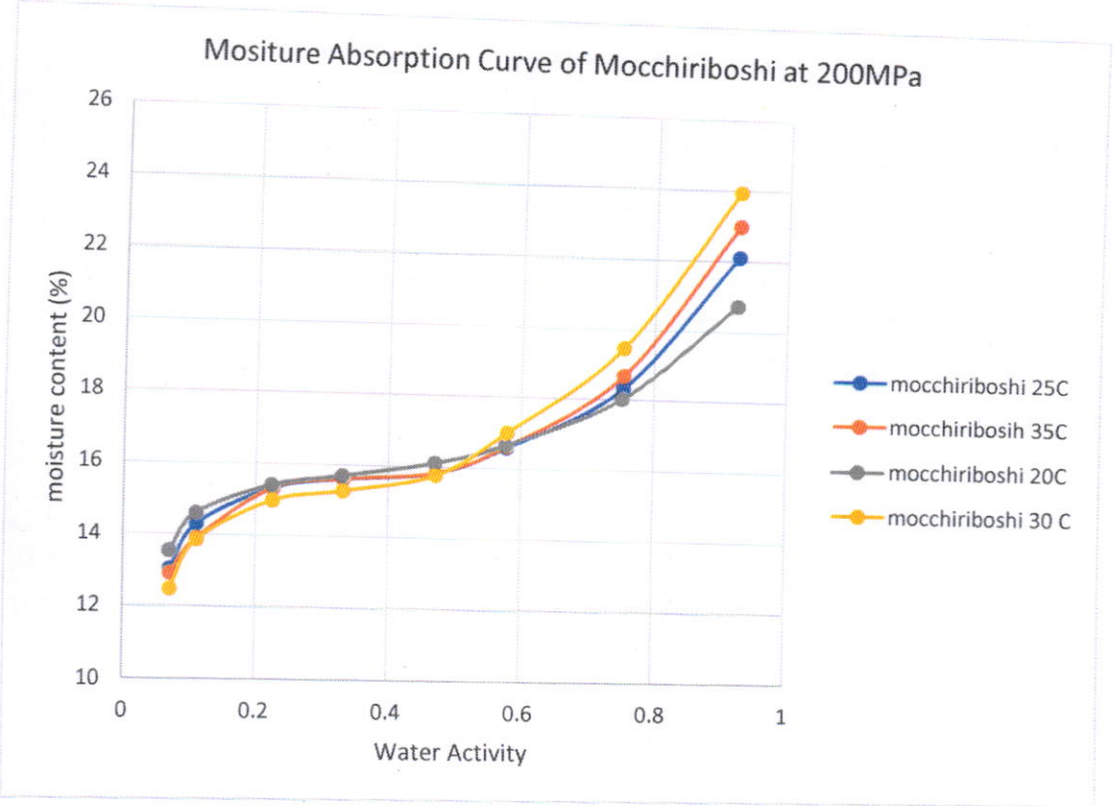


Figure 3.2 Moisture Absorption Isotherm of Mocchiriboshi under 200 MPa

As it is indicated in Figure 3.2, moisture absorption isotherms follows type 2 isotherms in all temperature. However, the moisture content is also varied in mocchiriboshi being treated under different temperatures. The moisture content of barley samples treated under 200 MPa is higher than that of barley samples without pressure treatment. The moisture content of the samples firstly increased quickly as the water activity became higher. However, the speed of increasing moisture content became stable from 0.4 to 0.6. When water activity was over 0.6, moisture content increased largely. The moisture absorption isotherms of barley flour with 200Mpa high pressure processing treatment followed strictly with sigmoidal shape as introduced in the above text. However, the moisture content differed as the incubation temperature changes. In the beginning, the moisture content was higher in barley samples with lower incubation temperature. After water activity was over 0.5, the moisture content of barley samples with higher incubation temperature tent to reach to higher amount.

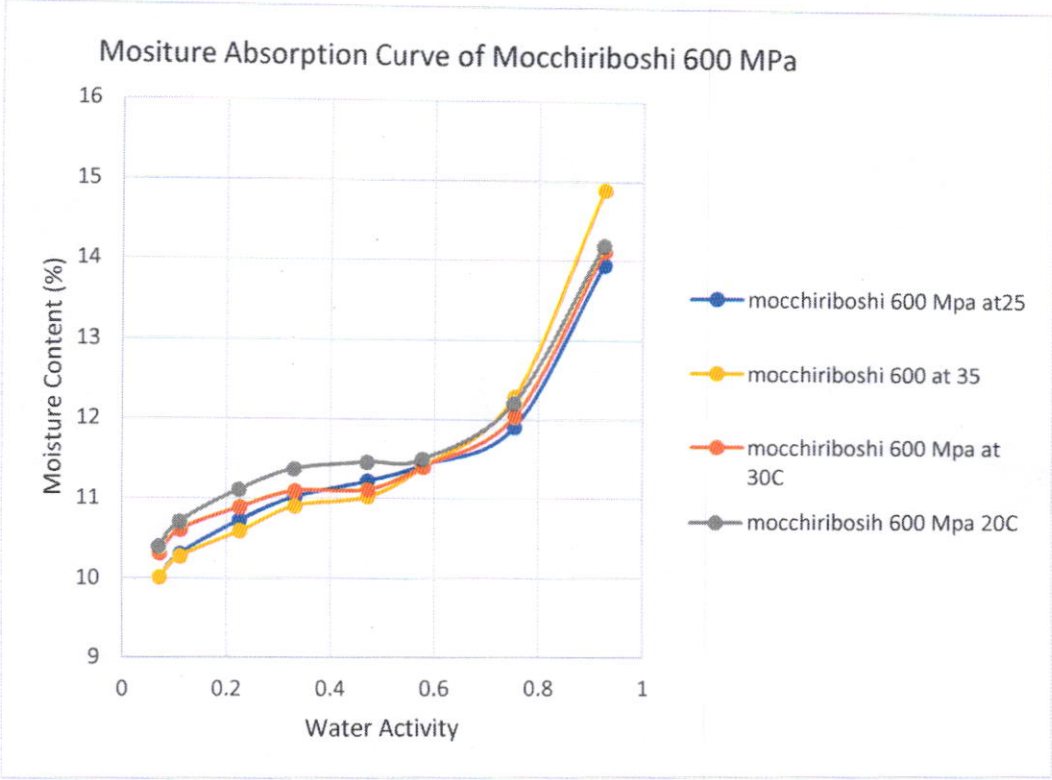


Figure 3.3 Moisture Absorption Isotherm of Mocchiriboshi under 600 MPa

As it is indicated in Figure 3.3, moisture absorption isotherms follows type 2 isotherms in all temperatures. Similar to water absorption isotherms of mocchiriboshi under different pressure treatments, the moisture content is also varied in mocchiriboshi being treated under different temperatures. The moisture content of barley samples treated under 600 MPa is lower than that of barley samples without pressure treatment or mocchiriboshi samples with 200 MPa pressure treatment. The moisture content of the samples firstly increased quickly as the water activity became higher. However, the speed of increasing moisture content became stable from 0.4 to 0.6. When water activity was over 0.6, moisture content increased largely. The moisture absorption isotherms of barley flour with 600Mpa high pressure processing treatment followed strictly with sigmoidal shape as introduced in the above text. However, the moisture content differed as the incubation temperature changes. In the beginning, the moisture content was higher in barley samaples with lower incubation temperature. After water activity was over 0.5, the moisture content of barley samples with higher incubation temperature tent to reach to higher amount.

**Discussion:**

In order to calculate moisture content at dry basis, it is important to determine the water and dry mass ratio (w/d ratio). A preexperiment was performed to determine the w/d ratio. The amount of barley flour was 1.00 gram. Sample was dried in a general oven under 105°C for two hours. Then the sample was removed from the oven and the put in room temperature for 30 minutes to cool down. After 30 minutes, the weight of sample was measured and recorded. Then the sample was dried in the general oven again. The same procedure was repeated until the weight of the sample did not change and remain in the constant range. The equation of w/d ratio was listed as follow, and w/d ratio equals 0.1:

$$\text{w/d ratio}=\frac{weight\ of\ water\ content}{weight\ of\ dry\ mass}$$

Moisture content is the quantity of water contained in a material. The amount of moisture in agricultural materials and food products affects the potential for storage without molding or deterioration from chemical reactions such as oxidation. It also affects the physical properties of the material. Particle density tends to decrease as the moisture content increases because the dry components such as starch and protein have a greater density than water. Products with higher moisture contents have higher thermal conductivities and lower electrical resistances because water is an excellent conductor of heat and electricity. Moisture content also affects force-deformation characteristics. Two methods are used to express the moisture content of materials: wet basis and dry basis moisture content. When performing these calculations, it is assumed that the sample loses only water and that the weight of the dry matter remains constant.

Wet basis moisture content ($M_w$) is described by the percentage equivalent of the ratio of the weight of water ($W_W$) to the total weight of the material ($W_t$).

$$M_w=W_w/W_t*100$$

Note that wet basis moisture content can range from 0 to 100 percent.

Wet basis moisture is used to describe the water content of agricultural materials and food products. When the term "moisture content" is used in the food industry it almost always refers to wet basis moisture content. One important example occurs in the grain industry where moisture content of whole grains is determined at each point in the marketing channel where the grain changes ownership.

Dry basis moisture content ($M_d$) is described by the percentage equivalent of the ratio of the weight of water ($W_W$) to the weight of the dry matter ($W_d$).

$$M_d = W_w / W_d * 100$$

Note that dry weight moisture content can range from 0 to very large percentages.

Dry basis moisture is most commonly used for describing moisture changes during drying. When a sample loses or gains moisture, the change in the dry basis moisture is linearly related to the weight loss or gain.

In this experiment, moisture content of dry basis was used. The equation is listed as follow:

$$\text{Moisture content (dry basis)} = \frac{weight\ after\ incubation \times 0.1}{weight\ before\ incubation - weight\ before\ incubation \times 0.1}$$

As it was indicated in the results, the shapes of the isotherms are characteristic of food with extremely high amount of starch, which sorb relatively small amount of water at low water activities and large amounts at high relatively humidity. The sharp increase in water content at high water activities is due to its high amount of starch, which the smallest unit is glucose. At low water activities, the physical state of the sugars are known to absorb some water than the crystalline materials. At water activities higher than 0.7, a leaching of sugar was observed, which was more pronounced at higher temperatures. At water activities lower than 0.6, the equilibrium moisture content of barley samples decreased significantly as the temperature was raised from 20 to 35°C in samples under all pressure treatments. However, the opposite effect was observed at higher water activities, and the barley flour samples absorbed more water at higher temperatures. It means that in the high humidity region the water activity at constant water content decreased as the temperature was raised.

At high water activities, the sugars are the determining factor of water absorption in barley flour samples, either treated with high pressure or treated with mild or even no pressure. The dissolution of sugars increased significantly as the temperature is raised, off- setting the opposite effect of temperature on the sorption of nonsugar solids. Similar effects of temperature have been observed by Audu et al (1978) on sugars, and Weisser et al. (1982) on sugar alcohols. Chinachoti and Steinberg (1984) found that sucrose added to starch gels increased sharply the sorption of water at water

activities higher than 0.85. A strong interaction of amorphous sucrose with gelatinized starch was detected by measuring the sorption isotherms of freeze-dried gels. Sugar-biopolymer interactions may have some effect on the observed adsorption isotherms of the dried raisins. Roman et al. (1982) found that temperature had the normal effect on the desorption isotherms of apples at 20" to 60°C. Compared to the isotherms of raisins, there was no crossing of the curves at high water activities, which may be due to the lower percentage of monosaccharides in the apples.

**Equations of absorption isotherms**

Six absorption models (Table 4.1) were tested to determine how well they fit high-pressure-processed barley flour samples.

Table 4.1 Absorption Isotherm Models

| Model | Equation |
|---|---|
| GAB (LABUZA et al., 1985b) | $M_{eq}=X_m\left[\frac{(C-1)Ka_w}{(1+(C-1)Ka_w)}+\frac{Ka_w}{(1-Ka_w)}\right]$ |
| Hailwood-Horrobin (HAILWOOD; HORROBIN, 1946) | $M_{eq}=a_w/\left(A+Ba_w+Ca_w^2\right)$ |
| Henderson (HENDERSON, 1952) | $M_{eq}=a_w/\left(A+Ba_w+Ca_w^2\right)$ |
| Peleg (PELEG, 1993) | $M_{eq}=k_1a_w^{n_1}+k_2a_w^{n_2}$ |
| Oswin (OSWIN, 1946) | $M_{eq}=A\left[a_w/(1-a_w)\right]^B$ |
| Chung-Pfost (CHUNG; PFOST, 1967) | $M_{eq}=A+B(\ln a_w)$ |

A number of theoretical and empirical equations found in the literature were tested for fitting experimental data of barley flour. The B.E.T equation was found unsatisfactory, evidently due to the fact barley is mostly comprised of starch, which changed considerable the shape of the isotherm.

Statistical analysis of an isotherm may be quantified through five standards: the coefficient of determination ($R^2$), the residual sum of squares (RSS), the standard error of the estimate (SE), the mean relative deviation (PE%), and the plot of residuals. In this experiment, the coefficient of determination and the mean relative deviation were

applied to evaluate whether the isotherm fit the mathematical models. The equation of the mean relative deviation and the coefficient of determination are listed as below:

$$PE\% = \frac{experimental\ M - predicted\ M}{experimental\ M}$$

$$R^2 = \frac{\sum\left(M_e - M_p\right)}{\sum M_e^2 \sum M_p^2}$$

Where $M_e$ is the experimental value, $M_p$ is the predicted value. The value of $R^2$ close to 1, and PE% below 5% indicates a good fit for practical purposes.

The six mathematical models presented in Table 4.1 were used to fit the experimental data of barley flour samples. The statistical results shown in Table 4.2 indicated that Henderson model presented the best adjustment under the given conditions. The determination coefficient ($R^2$) was very close to the unit and the PE was under 5%, indicating that this model is effective to describe the water sorption isotherm for barley flour samples (0 MPa, 200 MPa, 600 MPa) under given temperature.

Table 4.2 Estimated parameters of Henderson model for barley flours at different temperatures

| Temperature | Parameters of Henderson model | | | | |
|---|---|---|---|---|---|
| | A | B | PE (%) | $R^2$ | C |
| 20 | 356.814 | 1.864 | 2.049 | 0.998 | -1.664 |
| 25 | 3620.496 | 2.399 | 4.453 | 0.998 | -2.151 |
| 30 | 1816.316 | 2.040 | 3.106 | 0.996 | -1.539 |
| 35 | 6476.921 | 2.334 | 2.480 | 0.993 | -4.670 |

Furthermore, quantitative evaluation of experimental sorption data provided on the basis of the GAB model at certain temperature under 600 MPa is also good fit. Table 4.3 summarizes the estimated constants along with the mean relative (PE%) and coefficient of determination. At 25℃ and 35℃, the low value of PE% (3.5122~3.6767), and correlation coefficients $R^2$ (0.9843~0.9920) close to unity indicate that GAB model is good fit to the sorption data, and the estimated parameters were statistically acceptable.

Table 4.3 GAB Model Calculation for Barley at 600 MPa

| Equation | Equation constants | | | PE (%) | $R^2$ |
|---|---|---|---|---|---|
| GAB | a | b | c | | |
| 20C | 3.496 | 22.235 | 0.8057 | 6.0523 | 0.9894 |
| 25C | 4.112 | 282.846 | 0.8036 | 3.5122 | 0.9920 |
| 35C | 4.4966 | 71.404 | 0.8868 | 3.6767 | 0.9843 |

**Conclusion:**

According to the results obtained, moisture absorption isotherms of barley flours follows type 2 isotherms in all temperatures. . However, the moisture content is varied in mocchiriboshi being treated under different temperature. The moisture content of the samples firstly increased quickly as the water activity became higher. The shapes of the isotherms are characteristic of food with extremely high amount of starch, which sorb relatively small amount of water at low water activities and large amounts at high relatively humidities. The sharp increase in water content at high water activities is due to its high amount of starch, which the smallest unit is glucose.

The absorption isotherms of barley flour samples were best described by Henderson model. The determination coefficient ($R^2$) was very close to the unit and the PE was under 5%, indicating that this model is effective to describe the water sorption isotherm for barley flour samples (0 MPa, 200 MPa, 600 MPa) under given temperature.

GAB model can also describe the absorption isotherms under 600 MPa under 25°C and 35°C. The determination coefficient ($R^2$) was very close to the unit and the PE was under 5%.

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