FLOW AND PHYSICAL PROPERTIES OF DRY AND MOIST CORNMEAL POWDER

A Thesis

by

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ABSTRACT

Cornmeal powder is used in the food industry to manufacture a variety of food products. The knowledge of its flow behavior and physical properties is critical for efficient design of storage and handling processes. Factors affecting powder flowability are moisture content and the presence of conditioners.

The main goal of this study was to quantify the effect of moisture content and addition of a conditioner, on the flow properties of cornmeal powder. Flow characterization based on standard physical properties is not always accurate and needs to be complimented with the measurement of other properties. The flow properties of the cornmeal powder at different moisture content levels and concentrations of conditioner were measured. The moisture content at which the cornmeal was tested varied as 10.0%, 13.5% 17.0%, and 20.0% wet basis. The concentration of the conditioner, calcium stearate (caking agent classified at GRAS) was varied as 0.00%, 0.50%, 0.75%, and 1.00% wt/wt.

The optimum flow behavior characteristics of cornmeal powder were achieved at 0.50% wt/wt calcium stearate and 10.0% (w.b.) moisture content based on the flow function test. Overall, the sample flowability decreased with increase in moisture content which was characterized by the high values for Hausner's Ratio, Carr's Index, and angle of repose. The value of flow index (ff_c) obtained by the flow function test decreased from 6.47 to 3.82 with increasing moisture content indicating cohesive behavior of the cornmeal powder. Calcium stearate increased the flowability of cornmeal powder at 0.50% wt/wt, beyond which, the flowability was not affected significantly. Hygroscopicity of the samples was found to be in Class IV which means that the samples were very hygroscopic. The correlation coefficient for

Hausner's ratio, Carr's Index, and angle of repose were 0.91, 0.88, and 0.88, respectively, which showed a strong linear relationship with flow index that can be used to relate to the flowability of the cornmeal powder.

DEDICATION

This work is dedicated to my parents and sisters who have always loved me unconditionally and whose good examples have taught me to work hard for the things that I aspire to achieve.

I would not be the person I am today if it were not for you.

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NOMENCLATURE

A	constant (dimensionless)
a_w	water activity
B	constant (dimensionless)
C	GAB model parameter (dimensionless)
c_0	constant (adjusted to the temperature effect) (dimensionless)
ΔH_c	difference in enthalpy between mono-layer and multi-layer sorption (J mol^{-1})
ΔH_k	difference between the heat of condensation of water and the heat of sorption of the multilayer (J mol^{-1})
K	GAB model parameter (dimensionless)
k_0	constant (adjusted to the temperature effect) (dimensionless)
K_1, K_2	equation parameters (dimensionless)
n_1, n_2	equation parameters (dimensionless)
R	universal gas constant (8.314 J mol^{-1} K^{-1})
r	equation parameter (dimensionless)
T	temperature (K)
X	equilibrium moisture content (kg kg^{-1} dry solid)
X_0	mono-layer moisture content (kg kg^{-1} dry solid)
α	equation parameter (dimensionless)
β	equation parameter (dimensionless)

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CHAPTER I

INTRODUCTION

Powders are used widely in the food, pharmaceutical, and chemical industry. Several processes used in the food industry including blending, transfer, storage, feeding, compaction, and fluidization, involve powder handling (Prescott & Barnum, 2000). Powders can have sizes ranging from sub microns to as large as 3 – 6 mm in diameter, which makes them a very interesting material to study especially in the food industry where the applicability of powders is enormous.

One of the very basic properties of powders is its flowability, which is defined as the ease with which a powder will flow under a specified set of conditions. A powder with good flow characteristics is one that flows reliably without assistance. Operations such as blending, transfer, storage, compactions, and fluidization depend on good powder flowability (A. Bodhmage, 2006; Durney & Meloy, 1986; Emery, 2008). Designing and troubleshooting mass flow hoppers requires the measurement of powder flow (Abou-Chakra & Tüzün, 2000; Hegde *et al.*, 1985). Flowability of powders is affected by a number of factors including: particle size distribution, particle shape, chemical composition of the particles, moisture, temperature, etc. (Schulze, 2008). Moisture present in powders is one of the most potent factors that can affect the flowability of powders as it can change the behavior of the powder at varying moisture contents. Water present in food products affects the stability depending if it's bound or unbound water. Microbial growth is proliferated in environments rich in moisture. Furthermore, if the food product is hygroscopic in nature, it will absorb moisture that will result in a change in its flow properties ultimately giving rise to storage and handling issues.

Powders when stored in bin and silos may encounter flow problems such as rat-holing and arching. A rat-hole is a vertical hole formed at the outlet and extents to the top surface of the powder in the bin. Arching is problem when arches are formed at the outlet of the hopper or bin due to particle interlocking or due to an increase in the cohesive strength. Powders stored in the humid conditions may gain moisture, which would increase their cohesive strength due to the formation of liquid bridges. Powder discharge from the bin outlet is very important for the manufacturing of food products for quality control purposes.

Increase in the moisture content helps facilitate the strengthening of the interactions between the particles by forming liquid bridges. These bridges agglomerate the particles and result in caking of the powder, which impedes the flow. The behavior of powders can become erratically unpredictable if the moisture content within the stored powder keeps changing (Opaliński *et al.*, 2012). In starches, retardation of flow can be attributed to the crystalline and amorphous regions. During sorption, water molecules form hydrogen-bonds to the available hydroxyl group of the substrate i.e. those in the amorphous region and on the surface of the crystallites (Al-Muhtaseb *et al.*, 2004).

Physical, chemical, and environmental conditions influence the powder flowability and predicting the flow behavior based on a single factor may give inconclusive results. Physical properties such as particle size, shape, moisture content, density, etc. influence the powder flow with some properties affecting the flow more than others. Cohesiveness of powders is caused due to an interaction between the particles which becomes more pronounced in the presence of moisture. Powder flow is also affected by the equipment being used. Wall friction between the particles of the powder and the walls of the storage container may impede the flow by providing higher resistance to the particles.

Cornmeal powder is of particular interest to food engineers and scientists because of its widespread use in manufacturing food products. It is a meal made from dried maize, used for making tortilla, chips, bread, porridge, etc. (Bazua *et al.*, 1979; Ward *et al.*, 1998). This ingredient is critical when it comes to the food processing industry because many food products are made from cornmeal by the extrusion process. The relevant flow properties of cornmeal powder are: bulk density, particle density, angle of repose, particle size, flow index, cohesive strength, angle of internal friction, and angle of wall friction (Molenda *et al.*, 2002). Rat holing, arching, caking, segregation and flooding are some of the flow problems that are encountered in handling powders and so knowledge about the powder properties is very important from an economical and technical point of view (Aulton, 2013).

While a powder with good flow properties would be ideal for an application, oftentimes, we face situations where conditioners are required to increase the flowability of the powders. Conditioners are anticaking agents that prevent the powders from caking and thus retarding flow. They must be effective at low concentrations and is limited to a restricted level (FDA 1980). The concentration of these conditioners is usually varied from 1 to 3% with preference given to concentration of 1.00% or less (Hollenbach *et al.*, 1982; Peleg & Mannheim, 1973). Anticaking agents act as a barrier between particles of the powder thereby reducing the attractive forces that would cause an inhibition in the flow. They can also reduce the friction between the powder particles by acting as lubricants. A free-flow agent is added to powdered food products such as instant soups, spices and salt, to be able to flow freely and prevent formation of clumps. This is due to the cohesive forces between the particles. Caking depends on the strength of the cohesive forces, size of particles, surface structure, and size distribution. Following is true in most cases for powders: (a) the finer the powder, the stronger the cohesive forces; and (b) the more inhomogeneous the powder is in grain size distribution, the higher the tendency to clump.

1.1. Gap in knowledge

Flow behavior of various food powders including flour, starch, and sugars has been researched in the past but not enough information is available on the flow behavior of cornmeal powder (Ganesan *et al.*, 2008; Ghosal *et al.*, 2010; Teunou *et al.*, 1999). Most of the literature published on cornmeal is related to the extrusion process. Rheological parameters such as flow behavior index, apparent viscosity, and viscoelasticity of cornmeal dough have been widely researched but there is a scarcity of literature about the cornmeal powder as an ingredient itself (Padmanabhan & Bhattacharya, 1993). Knowledge of the flow behavior of cornmeal powder is required to understand if the ingredient being processed is flowing consistently and has not faced any significant chemical or physical changes on storage. Formation of clumps, which is called caking, that can be caused due to solid or liquid bridging, can impact the final product during the extrusion process (Al-Muhtaseb *et al.*, 2004; Mathlouthi & Roge, 2003) by affecting the feed flow rate. Hygroscopic classification of cornmeal powder is also required to predict the storage stability of cornmeal powder when stored at varying relative humidity.

1.1.1. Overall objective

This research investigated the impact of relative humidity on the cornmeal at constant temperature. Along with the change in flow behavior characteristics, the impact of different concentrations of anti-caking agent was also studied. Therefore, the overall objective of this research was to obtain useful data on cornmeal physical and flow properties to characterize the flow behavior and predict storage and processing stability. The overall objective was achieved by addressing the following specific objectives.

Specific objectives

1. Quantify the effect of moisture content and anti-caking agent (conditioner) concentration on the flow and physical properties of cornmeal

2. Develop moisture sorption isotherm to predict storage stability of the powder at room temperature.

3. Establish correlations among the different flow properties to be able to quantify powder behavior under specific conditions.

1.1.2. Central hypothesis

The central hypothesis for this study was that an increase in the moisture content of cornmeal powder would have a negative impact on its flowability by forming chemical and physical bonds between the particles of the powder. Therefore, addition of an anti-caking agent would help alleviate this issue by acting as a lubricant between powder particles. This behavior should be predictable using the developed correlations among flow and physical properties.

CHAPTER II

SYNTHESIS OF LITERATURE

2.1. Physical Properties of Powders

2.1.1. Moisture content and water activity

Moisture content is the quantity of water contained in a material. Moisture content of food powders is an important factor that influences the flow behavior. Increase in the moisture content leads to cohesion between the particles which may be formed due to liquid bridging (Peleg, 1977). As the moisture content increases, inter-particle interaction plays an important role in predicting the flow behavior (Pietsch, 1969). One of the many factors that might lead to liquid bridging is moisture content. Other factors being: melting, chemical reactions that liberate liquid, excessive liquid ingredients, etc.

Water activity (a_w) is defined as the partial vapor pressure of water in a substance to the standard state partial vapor pressure of water. It is considered a very important parameter in determining the stability of food materials. Water activity is directly related to relative humidity and can therefore be used to in predicting the stability of foods (Gebreselassie & Clifford, 2016). It is also very important in understanding the flow behavior of food powders as the increase in the water activity is related to the equilibrium moisture content of the food material, which is one of the factors that affect the flowability.

2.1.2. Bulk and tapped density

Bulk density is an important physical property of granulated materials because it helps determining their flowability. Bulk density is the ratio of the weight of the bulk of solid particles to the volume they occupy.

$$\rho_b = \frac{M_s}{V_t} \tag{2.1}$$

where ρ_b is the bulk density (kg/m^3), M_s is the mass (kg) of the solid occupying volume V_t (m^3).

The size, shape, moisture content, individual particle density, and surface characteristics are few factors affecting the bulk density (Sokhansanj *et al.*, 2006). Bulk density is influenced by the particle size distribution, moisture content, porosity, etc. This property is also influenced by the inter-particle interaction. It has been observed that an addition of conditioners increased the bulk density by lowering the inter-particle interaction (Peleg *et al.*, 1973). The bulk density of cornmeal is around 595 kg/m^3 (Molenda *et al.*, 2002).

Bulk density is an important quality indicator for granular materials when they are judged based on physical characteristics. It also plays a significant role when one needs to understand the flow dynamics and physical characteristics of granular materials (Trabelsi *et al.*, 2001).

The preparation, treatments, handling of the powder during processing and storage of the sample greatly affects the bulking properties of a powder. Depending on how the particles are packed, they can have a range of bulk densities and even the smallest disturbance of the powder bed can lead to a change in the bulk density of the sample. Therefore, it is very difficult to measure the bulk density of a powder with good reproducibility and with a specific record of how the determination was done (WHO, 2012).

Tapped density is the density of a material obtained by mechanically tapping a graduated cylinder containing the sample until very little of no further change in volume is observed. Once the initial powder volume or mass has been recorded, the measuring cylinder or vessel is tapped mechanically, and the new volume or mass readings are taken until little different volume or mass change is recorded. To achieve mechanical tapping, the cylinder or vessel is raised and then allowed to drop under its own mass in a specified distance. When tapping down, any possible separation of the mass should be minimized by selecting the devices that rotate the cylinder or vessel.

The inter-particulate interactions influencing the bulking properties of a powder also influence with powder flow, a comparison of bulk and tapped densities gives a measure of the relation between the two densities in a given powder sample. This comparison is used as an index of the ability of the powder to flow: Compressibility index or the Hausner's Ratio. The propensity of a powder to be compressed as described above, can be measured in terms of Compressibility or Hausner's Ratio. In particular, the two ratios are the measures of the powder's ability to settle and they allow the assessment of the relative importance of inter-particulate interactions. When a powder is free-flowing, such interactions do not hold huge significance, and the bulk and tapped densities have similar values. On the contrary, when there are poorer flowing materials, there are usually greater inter-particulate interactions and thus, it gives two different values of bulk and tapped densities.

Bulk density is an important parameter in determining the flowability of biological materials. It was suggested that the compressibility of a powder helps in indicating its tendency to flow. Hausner's ratio (HR) and Carr's Index (CI) are calculated using bulk density. Lower CI and Hausner ratios indicate better flow compared to higher values (Shah *et al.*, 2008) .

Table 2.1. Carr's index and Hausner's ratio for flow type. Adapted from Shah *et al.* (2008)

Carr's Index	Hausner's ratio	Flow type
CI <10	HR <1.11	excellent flow
11<CI<15	1.12<HR<1.18	good flow
16<CI<20	1.19<HR<1.25	fair flow
21<CI<25	1.26<HR<1.34	passable flow
26<CI<31	1.35<HR<1.45	poor flow
32<CI<37	1.46<HR<1.59	very poor flow
CI>38	HR >1.60	extremely poor flow

2.1.3. Particle density and apparent density

Particle density is defined as the weight of an individual particle per unit volume. This property measures the density of the particle matter excluding the air pores, hence it is called true density (Ileleji & Rosentrater, 2008; Oginni, 2014). The value of particle density is higher than bulk density due to exclusion of the air pores (Oginni, 2014). Similar to bulk density, particle density has an influence on the flow behavior of bulk solids. It has been suggested that a higher particle density can improve powder flow properties of a formulation (Hou & Sun, 2008). Contrary to this suggestion, Oginni (2014) suggested that reduction of pore spaces among particles will lead to higher density therefore the reduced flowability as the material will become compacted. The density of the solid material excluding the volume of any open and closed pores is called the true density of that material. Based on how the molecules are arranged in the material, the true density can be used to determine the closeness of a material to crystallinity (Dalla Valle, 1943). The measurements for True Density can be performed on excipients, blends, and monolithic samples such as tablets. The only difference between true density and apparent density is that in case of apparent density, the volume of closed pores is also included (Dalla Valle, 1943).

The amount of pore spaces or voids in a bulk of solid particles depends on the particle packing ability, which is determined by the shape, size distribution, and packing arrangements of the particles (Mongia & Ziegler, 2000). The bulk solids become less mobile as the packing ability of the materials reaches a maximum point. Packing fraction can be determined mathematically in terms of the ratio of the volume of the solids to the volume of the close-packed bed of solids for a given mass of particulate material (or bulk density/true density). The maximum packing fraction of solids for a specific particle size distribution can be increased by adding particles with sizes corresponding to the dimensions of the voids in the packing bed. The ratio of the particle diameters, number of distinct sizes (modality) and the volume fraction of the small and large particle components decide the extent of reduction in the void volume (Mongia *et al.*, 2000).

2.1.4. Porosity

Porosity is a measure of the void spaces in a material, and is a fraction of the volume of voids over the total volume with values that range between 0 and 100% (Oginni, 2014; Rahman *et al.*, 1996). It can be expressed as the percentage of voids in a bulk solid (Ganesan *et al.*, 2008):

$$\emptyset = \left(\frac{V\text{-}V_p}{V}\right) \times 100\ (\%) \qquad (2.2)$$

where $\emptyset$ is porosity (%); V is bulk volume of the bulk (m^3); and V_p is particle volume of the bulk (m^3). Generally, more spherical powders have better flow properties when compared to elongated particles (Hou *et al.*, 2008). A porosity of around 0.4 refers to spheroid particles.

Irregular and very small particles have high porosities (Oginni, 2014; Woodcock & Mason, 2012).

The mechanical and textural properties also play an important role when it comes to the food porosity property. In case of fresh apples, Vincent (1989) found that torsional stiffness (0.5–7 MPa) varies with the porosity (0.83–0.54). On similar basis, when studies were conducted for potato, a relationship between loss modulus and porosity was observed. For some food, such as extruded starch, porosity is highly correlated with shear strength or other mechanical properties (Bhatnagar & Hanna, 1997; Rahman, 2001). The fried snack foods or extruded snack foods have a high correlation between porosity and crispiness. The agglomerate strength of dried foods is mostly dependent on porosity. If the apparent density of the agglomerate is high and the porosity if low, it results in a stronger agglomeration. Apart from porosity, adhesion or binding forces of particles in the matrix, the structure of the matric also affects the mechanical strength of a sample (Rahman, 2001). In case of low-moisture foods, the stiff-walled cells are filled with air and with liquid in high-moisture foods. The cell walls burst in a serial manner when sufficient force is applied during crushing by bite. Thus, vibratory sensations by sound are produced when cellular or porous foods are crushed. Depending on the life and end use of a food product, the pores can be desirable or undesirable. For products such as cereals, where a long bowl life is desirable, a crust product that prevents moisture absorption maybe preferred. On the contrary, for products such as dehydrated vegetables in instant noodles, high pores are preferred for their fast rehydration (Rahman, 2001).

2.1.5. Angle of repose

Angle of repose is defined as the angle between the horizontal and the slope of a heap of granular material dropped from some designated elevation (Figure 3.1). This parameter is often used to characterize flowability. In this, bulk solid is flowing onto a flat surface and forming a pile. As soon as the pile is formed fresh bulk solid slides erratically along the pile surface (Schwedes, 2003). It has been suggested that angles of repose below 30° indicate good flowability, 30°-45° some cohesiveness, 45°-55° true cohesiveness, and >55° sluggish or very high cohesiveness and very limited flowability (Carr, 1965, 1969; Geldart *et al.*, 2006).

The angle of repose is a small angle on the order of 35° or less produced in the form of a cone by free flowing and granular materials when poured through a funnel on a flat surface. On the contrary, cohesive powders have a higher angle of repose which is on the order of 55° or higher in which case the powder cone can also have an irregular and distorted shape (Peleg, 1983). The angle of internal friction and the angle of repose are entirely different. When cohesive powders are considered, due to their inter-particle forces, they are able to maintain a steep, conical shape. Friction plays a very small in determining the angle of repose. Thus, the angle of repose can give a credible measure of flowability of powders but poses a problems of getting consistent results due to the varying type of the cones formed due to factors such as fall height, handler, test method, etc. The knowledge of the angle of repose and of the powder's bulk density can play a significant role in order to calculate the volume and weight of a powder heap when scooped with a spoon in case of instant dry beverages or soups (Peleg, 1983).

2.1.6. Moisture sorption isotherms

Moisture sorption isotherms describe the thermodynamic relationship between equilibrium moisture content and water activity at a constant pressure and temperature. Understanding the sorption characteristics of food products is important in designing equipment for storages, handling, drying, etc., designing packaging, product stability, and shelf life prediction and estimation (LEMUS M, 2011). The amount of moisture present in a food material can be classified as bound water, intermediate water, or free water. As the amount of free water increases, the stability of the products decreases. This decrease can be in the form of shelf life or flowability. Water activity is defined as the ratio of water vapor pressure in the system and the pure water vapor pressure at a constant value of pressure and temperature.

Sorption isotherms can be generated from an adsorption process or a desorption process; the difference between these curves is defined as hysteresis. (LEMUS M, 2011).

The knowledge of sorption isotherms for particular powders is important in designing systems that can process powders with minimum difficulty storage condition and even packaging systems. The moisture content of the sample when it comes in vapor pressure equilibrium with its surrounding is called the equilibrium moisture content (EMC) and is used to determine the sorption isotherms

The term equilibrium relative humidity (ERH) or water activity (A_w) is widely used in determining the stability of food materials during storage. This parameter describes to what degree water is bound in a food product and how its availability is going to impact the stability. The implications of ERH are more than just stability because it is used to aid engineers design process systems and equipment (Damodaran *et al.*, 2007; Debnath *et al.*, 2002; Fennema, 1976).

Water sorption isotherm equations are used in predicting the water sorption properties of foods but are not very helpful in explaining the interaction of water with the food components (Al-Muhtaseb *et al.*, 2004). Since foods are a complex topic to study, it is extremely difficult to use just one equation to give accurate results. Therefore, different mathematical equations can be used to fit the data and suggest the model that fits best. Examples of common predictive equations to describe food materials isotherms are given in Table 2.2.

Table 2.2. Mathematical models for predicting sorption isotherms

Model	Expression	
Mod-BET (Aguerre *et al.*, 1989)	$X=\frac{X_0Ca_w}{[(1-a_w)(1-C\ln(1-a_w))]}$	(2.3)
Hasley (Halsey, 1948)	$X=[\frac{A}{(\ln(1/a_w)}]^{\frac{1}{B}}$	(2.4)
Smith (Smith, 1947)	$X=A+(B\log(1-a_w))$	(2.5)
Henderson (Henderson, 1952b)	$X=[\frac{-\ln(1-a_w)}{A}]^{\frac{1}{B}}$	(2.6)
Oswin (Oswin, 1946)	$X=A(\frac{a_w}{(1-a_w)})^{B}$	(2.7)
Ferro-Fontan (Fontan *et al.*, 1982)	$X=[\frac{\gamma}{\ln(\frac{\alpha}{a_w})}]^{\frac{1}{r}}$	(2.8)
Guggenheim-Anderson-de Boer (Van den Berg & Bruin, 1978a)	$X=\frac{X_0CKa_w}{[(1-Ka_w)(1-Ka_w+CKa_w)]}$	(2.9)
	$C=c_0\exp(\frac{\Delta H_c}{RT})$	(2.10)
	$K=k_0\exp(\frac{\Delta H_k}{RT})$	(2.11)
Peleg (Peleg, 1993)	$X=K_1a_w^{n_1}+K_2a_w^{n_2}$	(2.12)

2.1.7. Hygroscopicity

Food powders are generally hygroscopic in nature and the extent of hygroscopicity differs from powder to powder. Hygroscopicity is the ability of powders to absorb moisture from the environment at high relative humidity (Jaya & Das, 2004; Pereira Canuto *et al.*, 2014). Powders that are hygroscopic in nature will experience an increase in their moisture content (MC) if they are placed in a high humidity surrounding (Juarez-Enriquez *et al.*, 2017). In case of dehydrated food materials, water is adsorbed onto the boundary surface of a dry solid material since the sorption takes place at the solid-liquid interface. The region after monolayer saturation is reached is used to classify the moisture uptake or the hygroscopicity of the material. In materials that undergo monolayer adsorption, after reaching the saturation point, the curve plateaus in the region II which gives an indication of the hygroscopicity of the material. This result will affect the flow properties and some powders will start to cake with increase in their MC. The purpose of hygroscopicity classification is to determine the stability of cornmeal powder on storage. It is also important to understand the hygroscopicity for packaging purposes. Under unfavorable condition, cornmeal powder can change its physical form rapidly.

2.1.8. Particle shape and size distribution

Particle size measurement and the determination of particle size distribution are essential to anyone dealing with particulate systems. Particles have different shapes and are involved in different processes.

Foods materials are mostly in the form of powder before, during or after processing. The bulk density, compressibility, and flowability of a food powder are highly dependent on particle size and size distribution (Barbosa-Cánovas *et al.*, 2012). Free flowing powders that have differences in the particle size may experience segregation. For that reason, particle size is considered to be one of the major factors affecting the flowability of food powders.

Methods to characterize particle size are classified as direct and indirect. Some of the most common direct methods include image analysis and optical methods (Althaus, 2009b). Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) are used to measure very fine sizes. Even though automatic image analysis systems offer many advantages, its difficulty in differentiating between clusters and single particles poses a limitation.

The oldest method of indirect particle size characterization is sieving. Manual and mechanical methods for sieving exist as well as dry and wet sieving systems (Barbosa-Cánovas *et al.*, 2012). Automatic systems have also been developed.

Particle shape and size influence some of the properties of powders including packing efficiency and powder flow (Sandler & Wilson, 2010). Fine powders usually have a very high surface-to-mass ratio which makes them cohesive as compared to coarse particles. It has been seen that particles smaller than 100µm are cohesive whereas particles greater than 250µm are generally free flowing (Aulton & Taylor, 2017).

2.2. Flow properties of food powders

2.2.1. Flow function

The flow function is defined as measure of the internal resistance to flow of a powder, often manifested in its ability to form a blockage in a hopper or feeder (Berry *et al.*, 2015). This property was first introduced by Jenike using a Jenike's shear cell (Jenike, 1964). By measuring the required shear force for various vertical loads, one can develop a relationship describing the cohesive strength of the powder as a function of the consolidating pressure which is the process of applying a normal and a shear stress to a bulk solid to move the particles together, in order to observe any increases in its cohesion, bulk density, etc. Cohesive strength is measure of the strength retained by a powder after it has been compacted to a given consolidation level. This relationship, also known as a flow function, can be analyzed to determine the minimum outlet diameters for bins, press hoppers, and blender outlets, to prevent arching and ratholing(Prescott *et al.*, 2000). Figure 2.1 shows two types of flows commonly encountered during powder discharge from the hopper outlet i.e. mass flow and core flow. Hoppers are conical sections at the end on the storage vessel. In mass flow, material going in first, comes out first whereas in core flow, the material that going in last, comes out first. Core flow may lead to a common problem call ratholing (Figure 2.2). In ratholing, the material on the sides of the wall remains stationary and a hole is created which forces the material entering from the top to directly discharge from the hopper outlet. Sometimes, due to the cohesiveness of the powders, the powder particles may block the exit due to forces between them and form an arch. This problem is referred to as arching (Figure 2.2). Table 2.3 and Figure 2.3 give the value for flow index (ff_c) which gives a numerical interpretation to the flow function of different powders. Powders with relatively higher flow index have better flowability.

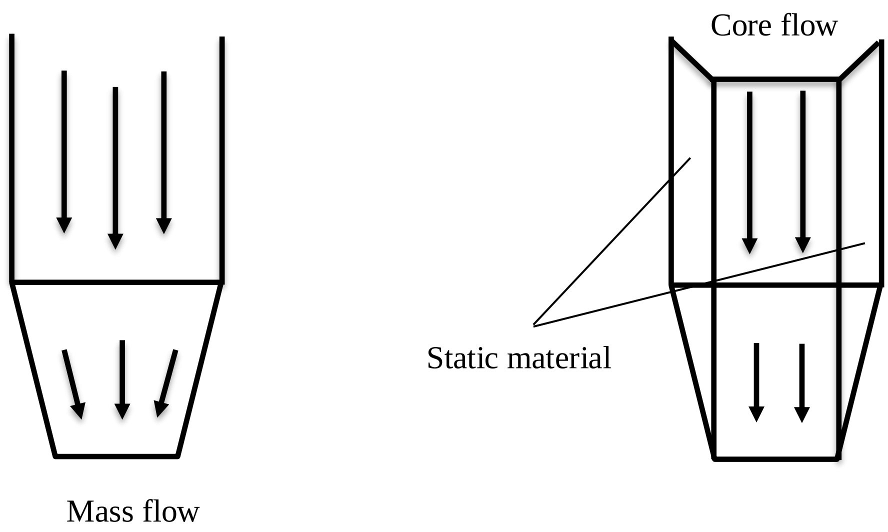

Figure 2.1. Mass flow and core flow in hoppers

Figure 2.2. Rat holing and arching at hopper outlet

A simple definition of powder flowability is the ability of a powder to flow. By this definition, flowability is sometimes thought of as a one-dimensional characteristic of a powder, whereby powders can be ranked on a sliding scale from free- flowing to non-flowing (Prescott *et al.*, 2000).

Since flowability is not an inherent property of a material it can never be expressed as a single value or index. It, however, is the result of the combination of material physical properties that affect material flow and the equipment used for handling, storing, or processing the material (Goodridge *et al.*, 2012). Equal consideration must be given to both the material characteristics and the equipment. Depending on the type of hopper material and design, the same powder may flow well in one hopper but might experience reduced flowability in another. Therefore, a more accurate definition of powder flowability is the ability of a powder to flow in a desired manner in a specific piece of equipment. Flowability is a factor for several processes in the food and pharmaceutical industry as mentioned by Prescott *et al.* (2000):

- powder storage can be affected due to the formation of aggregates (caking) in silos and tanks
- separation of a small quantity of powder from the bulk
- blending process in which the consistent flow of powder is required for product quality uniformity
- compaction processes (e.g., roller compaction and tablet compression)
- fluidization, whether for assisting flow or for fluidized-bed processing such as granulation and drying
- powder flow may be used for quality control (Prescott *et al.*, 2000).

Table 2.3. Flow function ff_c (adapted (Schulze, 2008)

Flow function	Flow type
$ff_c < 1$	not flowing
$1 < ff_c < 2$	very cohesive (to non-flowing)
$2 < ff_c < 4$	cohesive
$4 < ff_c < 10$	easy flowing
$10 < ff_c$	free-flowing

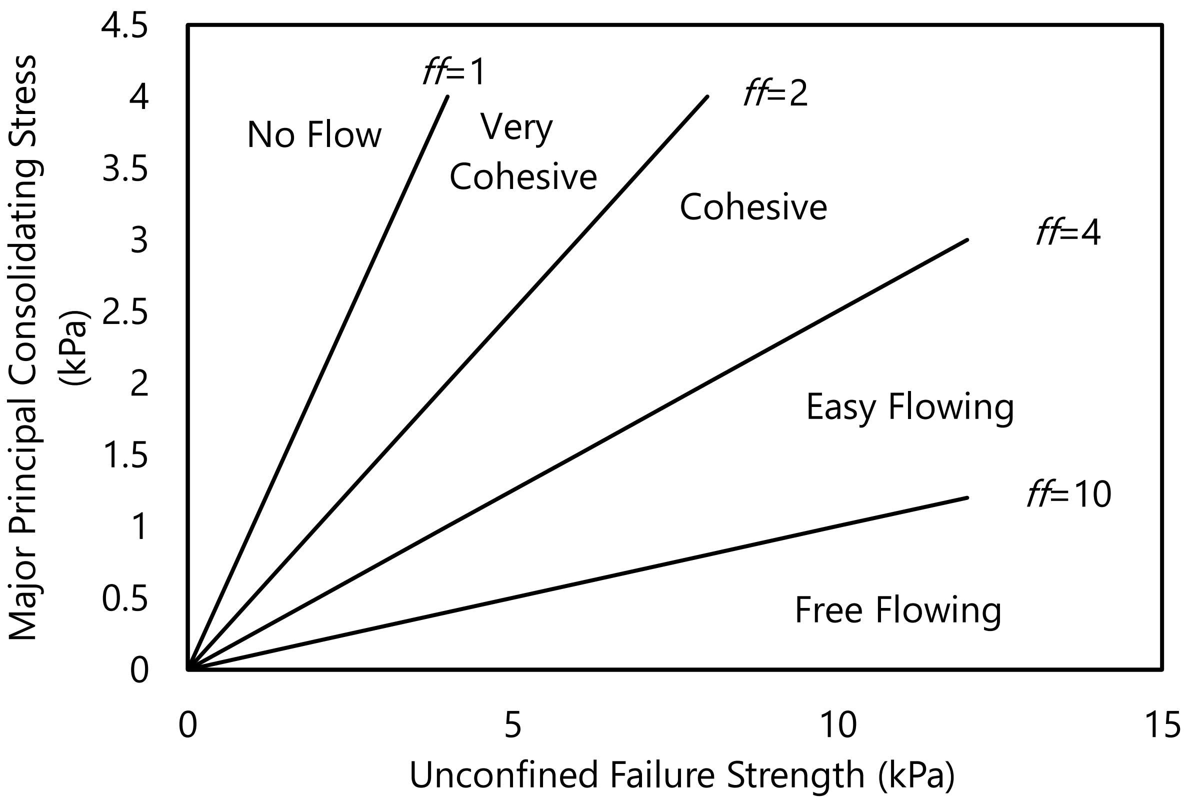

Figure 2.3. Flow function and line of constant flowability. Adapted from Schulze (2001)

2.2.2. Angle of internal friction

The angle of internal friction is a measure of the friction between the powder particles as they slide against each other given by equation 3.13. It is well defined for non-cohesive powders as compared to cohesive powders. For complex powders, the angle of internal friction may depend on the normal stress (Peleg, 1977). Internal friction is influenced by parameters such as: particle surface friction, shape, hardness, size, and size distribution (Ganesan *et al.*, 2008). It has been noted that the cohesion of powders increases drastically with moisture. This can be explained based on the following mechanisms:

- The liquid layer formed around the particles acts as a lubricant.
- Solubility of the parts of the particles surface smooth their shape thus eliminating rough points that promote friction (Fitzpatrick *et al.*, 2004; Peleg, 1977).

In Figure 2.4, the symbol Φ_e is the angle of internal friction of the effective yield locus (Althaus, 2009b). A low value of internal friction angle refers to a low friction between the particles.

Φ_{sf} represents the angle of internal friction at steady-state flow and can be determined graphically by drawing a line through the origin and the pre-shear point (Althaus, 2009a). A low value represents less friction between the particles and the wall of the container.

The angle of internal friction is well-defined in non-cohesive powders. For cohesive powders, several different definitions have been suggested. It should be mentioned again that for irregular or complex powders the angle of friction may depend on the normal stress. These show that moisture absorption drastically increased the cohesion and the tensile strength resulted in a significantly smaller angle of friction. It should also be mentioned that in cohesive food powders friction plays only a minor role in the obstruction to flow if compared to inter particle forces (Peleg, 1977).

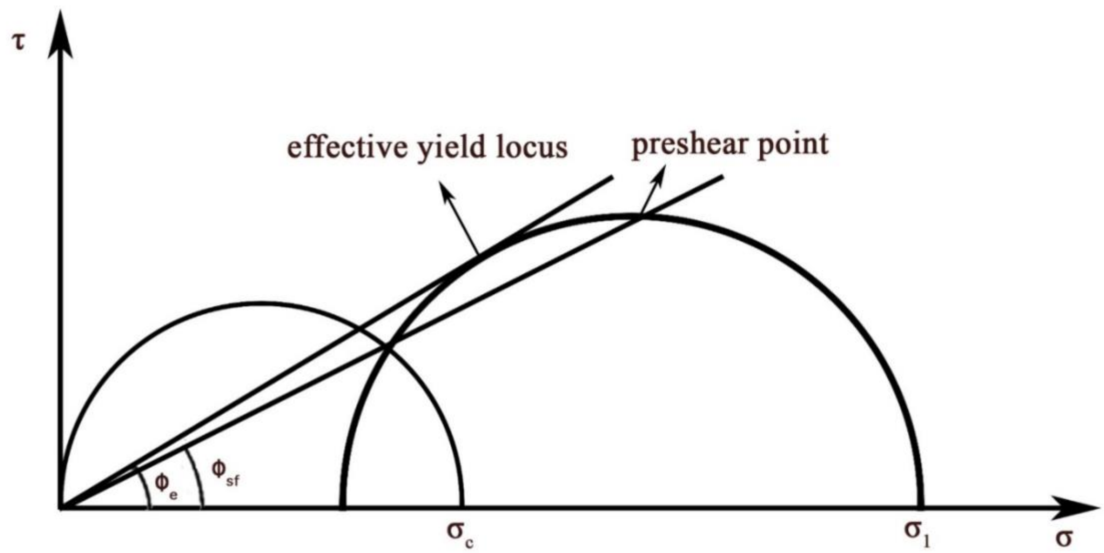

Figure 2.4. Flow parameters defined by the individual yield locus. Adapted from Althaus (2009a)

2.2.3. Angle of wall friction

The angle of wall friction is a measure of the friction between the bulk solid particles and the wall material given by equation 3.14. It is an important parameter in the designing and operation of hoppers, silos, and storage and discharge chutes (Ganesan *et al.*, 2008; Iqbal & Fitzpatrick, 2006). Knowledge of the wall friction angle helps in deciding whether to use a liner or to have the inner wall surface polished. A low value of angle of wall friction would mean that no surface finishing is required and the material flows easily without facing much resistance from the container wall. Wall friction is influenced by various factors, such as bulk solid properties, wall surface characteristics, and handling conditions (Ganesan *et al.*, 2008; Prescott *et* *al.*, 1999). Savage (1967) observed that the wall friction was more influential than the angle of internal friction in reducing the flow rate for hoppers with small half angle.

Used in a continuum model, wall friction (particles sliding along a surface) is expressed as the wall friction angle or the coefficient of sliding friction. As the coefficient of sliding friction in- creases, the hopper or chute walls must be steeper for a powder to flow along them. The friction coefficient can be measured by sliding a sample of powder in a test cell across a stationary wall surface using a shear tester. A plot of the measured shear force as a function of the applied normal load generates a relationship known as the wall yield locus. This flow property is a function of the powder handled and the wall surface in con- tact with it. Variations in the material or the wall surface finish can have a dramatic effect on the resulting friction coefficient. Wall friction can be used to determine the hopper angles required to achieve mass flow (Prescott *et al.*, 2000) .

CHAPTER III

MATERIALS AND METHODS

3.1. Materials

Cornmeal powder was chosen for this study because of its widespread use in the food industry as a major ingredient and the lack of engineering data on the flow behavior of this material during storage. Quaker Yellow Cornmeal (The Quaker Oat Company, Chicago, IL, USA) was purchased at a local market (HEB, College Station, TX, USA) and stored at room temperature (25°C) in sealed glass jars until further use. Calcium Stearate (Spectrum Chemical Manufacturing Corp., New Brunswick, NJ, USA) was used as a flow conditioner (anti-caking agent) and stored at room temperature (25°C).

3.2. Experimental design and Statistical analysis

The experimental design for characterization of the flow behavior of cornmeal powder consisted of two factors at four levels each (Table 3.1). The factors considered for this experiment were (1) moisture content and (2) concentration of conditioner.

Statistical analysis was conducted using JMP Pro 13 (SAS, NC, USA) software to test for ANOVA. Students t-test was done to compare the means of the values at different moisture content and concentration of calcium stearate and their significance was determined at ($\alpha <0.05$). JMP Pro 13 was also used in predicting models for moisture isotherms and graphing the data.

Table 3.1. Experimental design to study the flow behavior of cornmeal powder

Experiment	Factors	
	Moisture content (% w.b.)	**Anti-caking agent (Calcium Stearate, % wt/wt)**
1	13.5	0.75
2	17.0	0.75
3	10.0	0.50
4	17.0	0.00
5	17.0	0.50
6	17.0	0.00
7	17.0	0.50
8	17.0	0.00
9	13.5	1.00
10	13.5	0.75
11	20.0	1.00
12	10.0	0.75
13	10.0	0.00
14	13.5	0.50
15	13.5	1.00
16	13.5	0.00
17	20.0	1.00
18	13.5	0.00

Table 3.1. Continued

Experiment	Factors	
	Moisture content (% w.b.)	Anti-caking agent (Calcium Stearate, % wt/wt)
19	13.5	0.50
20	20.0	1.00
21	10.0	0.00
22	20.0	0.50
23	13.5	0.75
24	20.0	0.50
25	17.0	1.00
26	17.0	1.00
27	10.0	0.75
28	13.5	1.00
29	10.0	0.50
30	10.0	0.50
31	10.0	1.00
32	13.5	0.50
33	17.0	0.50
34	20.0	0.00
35	20.0	0.75
36	17.0	1.00

Table 3.1. Continued

Experiment	Factors	
	Moisture content (% w.b.)	**Anti-caking agent (Calcium Stearate, % wt/wt)**
37	20.0	0.75
38	10.0	1.00
39	10.0	0.75
40	20.0	0.75
41	20.0	0.50
42	10.0	1.00
43	13.5	0.00
44	10.0	0.00
45	17.0	0.75
46	20.0	0.00
47	20.0	0.00
48	17.0	0.75

3.3. Physical and Flow Properties of Powders

3.3.1. Moisture content

The moisture content of the cornmeal samples was varied from 10.0% to 20.0% (w.b.) and determined by the oven dry method (AOAC, 1925), modified for use. The modification consisted of drying the sample at 105°C for 24 hours instead of at 130±3°C for 5 hours for complete removal of moisture of the samples without degradation. A calculated weight of Reverse Osmosis (RO) water from a pipet was added to the samples depending on the moisture content to be achieved and the moisture throughout the sample was distributed by careful stirring manually for at least 5 minutes to achieve uniform moisture distribution (Eaves & Jones, 1972). The samples were left overnight until they reached equilibrium before testing. Approximately 4-5 g of sample were placed in round, flat bottomed dishes with a tight-fitting slip-in cover previously dried at 50°C in an air oven (VWR, Radnor, PA, USA) for 24 hours, cooled in a desiccator (Vacuum Desiccator, VWR, Radnor, PA, USA) and weighed with cover using an analytical balance (Sartorius AC 210 S MC 1, Germany) soon after attaining room temperature (25°C). The cover was leaned against the dish and placed in an air oven (VWR, Radnor, PA, USA) at 105°C. The samples were allowed to dry for 24 hours for complete removal of moisture (AOAC, 1925) and then transferred to the desiccator with the cover placed to close the dish and allowed to cool to room temperature. Three repetitions were done for each sample and the moisture content on a wet and dry basis was calculated as:

$$\text{MC (\% w.b.)} = \frac{W_w}{W_s} \times 100 \tag{3.13}$$

$$\text{MC (\% d.b.)} = \frac{W_w}{W_d} \times 100 \tag{3.14}$$

where W_w is the weight of water in the sample (kg), W_s is the weight of the sample (kg), and W_d is the weight of the dry sample (kg).

3.3.2. Moisture sorption isotherm

Moisture sorption isotherms were obtained using the standard procedure with saturated salt solutions listed in Table 3.2 at 25°C. The temperature at which the experiment was conducted was chosen based on the variation of the room temperature in a day. The incubator was able to maintain 25°C consistently. The samples were prepared by drying in a vacuum oven (Lab-Line Instruments, Inc., IL, USA) for 6 hours at 70°C. Approximately 5 grams of sample was placed in a petri dish and kept in five-inch desiccators (Thermo Scientific, Waltham, MA) containing a particular salt solution. The dried samples in the desiccator were placed in an incubator (Curtin Matheson Scientific, Inc., Houston, TX) which was maintained at 25°C. The weight of the samples was determined at two-days intervals for about a week until they reached equilibrium (Debnath *et al.*, 2002). The moisture content was determined using equations (3.1) and (3.2) above. Relative humidity values were converted to water activity by dividing by 100. Three readings for each sample were taken to determine the moisture content.

Table 3.2. Humidity fixed points of binary saturated aqueous solutions at 25°C (Greenspan, 1977; Labuza *et al.*, 1985) used for development of moisture isotherms.

Saturated Salt Solution	Relative Humidity (%)
Lithium Chloride	11.3
Magnesium Chloride	32.8
Potassium Carbonate	43.2
Sodium Bromide	57.6
Sodium Chloride	75.3
Potassium Chloride	84.3
Potassium Sulphate	97.3

The data obtained was fitted to several mathematical models including two parameter relationships: Halsey Oswin (Halsey, 1948), Henderson (Henderson, 1952a), Model-BET (Aguerre *et al.*, 1989) and Smith(Smith, 1947), three parameter equations: GAB (Van den Berg & Bruin, 1978b), and Ferro-Fontan (Fontan *et al.*, 1982) and four parameter equation: Peleg (Peleg, 1993) (Al-Muhtaseb *et al.*, 2004) as given in Table 2.2 of Chapter 2.

3.3.3. Hygroscopicity

Hygroscopicity of cornmeal powder was determined by the amount of moisture absorbed by the samples when exposed to varying relative humidity for five days at 25°C. A modified version of the method by Callahan *et al.* (1982) was used in this study. The method was modified so that the classification could be done with minimum amount of sample without mold growth.

The degree of hygroscopicity is defined as the ratio of change in equilibrium moisture content when subjected to a give change in water activity (eq. 3.3) and was quantified by observing the shape and obtaining the slope from the moisture isotherms of the different materials as shown in figure 3.1. The S-shaped curve obtained was divided into three regions. Region II, which consisted of multilayer adsorption was used to find the rate of water uptake for the cornmeal samples. Degree of hygroscopicity of the samples was determined using the slope of the linear part of region II of the moisture isotherms prepared. Materials with high value of degree of hygroscopicity have high water uptake potential and would therefore be classified as highly hygroscopic. Since hygroscopy is a qualitative rather than quantitative term, it is difficult to characterize materials based on the degree of hygroscopicity, but the knowledge of this property is helpful in distinguishing the hygroscopicity when comparing among samples. The amount of moisture absorbed by the sample on achieving equilibrium moisture content was used in classifying the sample based on the Table 3.3. The initial and final weights were recorded using an analytical lab balance (Sartorius AC 210 S MC 1, Germany).

$$\text{Degree of Hygroscopicity} = \frac{\Delta X}{\Delta a_w} \tag{3.3}$$

where Degree of Hygroscopicity is in g H_2O/100 g dry sample/a_w, ΔX is the change in the EMC (d.b.) for a given change in water activity (a_w) in the sorption isotherms

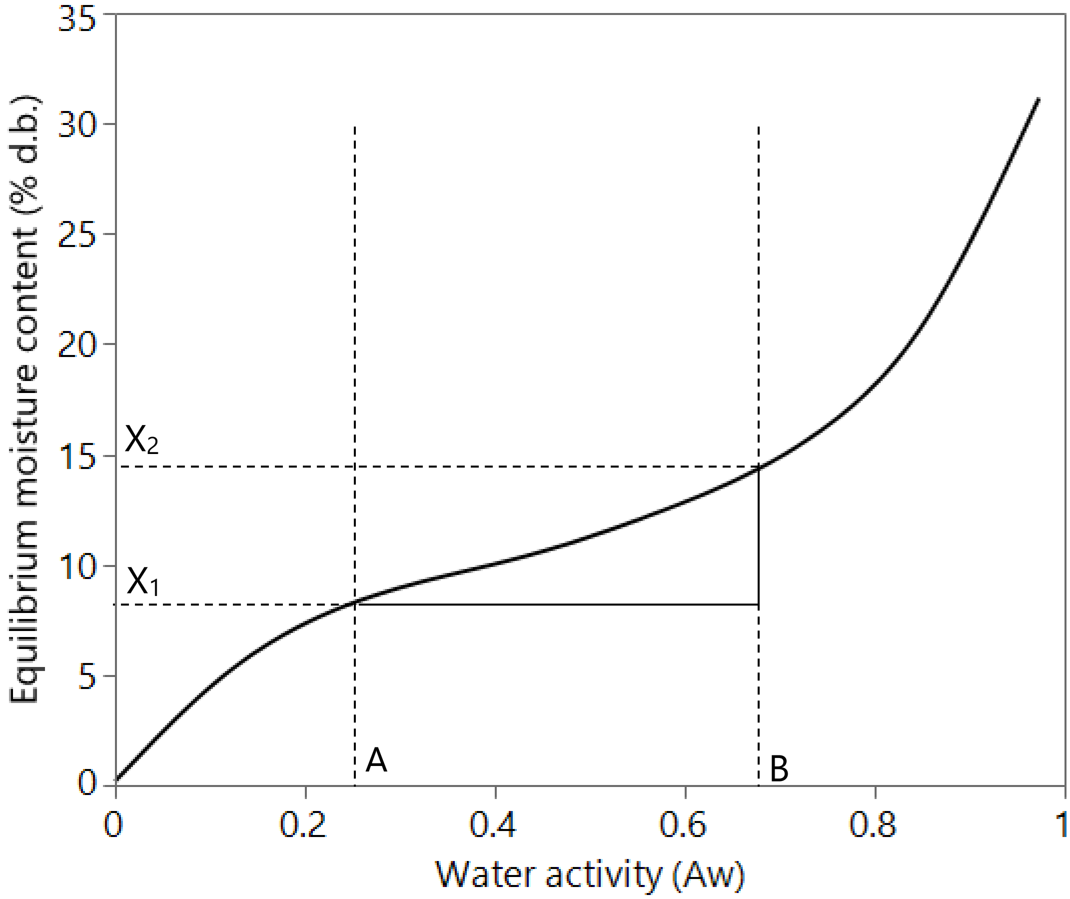

Figure 3.1. Measuring degree of hygroscopicity (g H_2O/100 g dry sample/a_w) based on the linear region in the region II of moisture sorption isotherm

Table 3.3. Hygroscopicity classification for powder based on the relative humidity using desiccators (Adapted from Callahan *et al.* (1982))

Class	Classification
Class I	No moisture increase at R.H. < 90%. Increase in M.C. (d.b.) after one week above 90% R.H. is less than 20%.
Class II	No moisture increase at R.H. <80%. Increase in M.C. (d.b.) after one week above 80% R.H. is less than 40%.
Class III	M.C. does not increase above 5% after storage at R.H. < 60%. Increase in M.C. (d.b.) after one week above 80% R.H. is less than 50%
Class IV	M.C. increase may take place at low R.H of 40-50%. Increase in M.C. (d/b.) after storage for one week above 90% R.H. may exceed 30%.

3.3.4. Bulk density

Bulk density was measured according to the specifications of ISO 3923/1 standard as mentioned by Wong (2000). Approximately 50g of powder at 25°C was poured in a conical funnel with 1-inch outlet port which was blocked at the discharge outlet. A graduated cylinder was placed below the funnel discharge outlet. The powder was filled in the graduated cylinder on the removal of the plug which was placed to block the outlet of the funnel. Excess powder was removed and three replicates for bulk density were conducted using the ratio of mass of the powder and the volume of the powder in the cylinder as,

$$\text{Bulk density} = \frac{W_s}{V_s} \tag{3.4}$$

where W_s is the weight of the sample (kg), and V_s is the volume occupied by the sample (m^3).

3.3.5. Tapped density

The tapped density was measured by tapping the graduated cylinder 100 times on a bench so that the powder settles down and no more settling is visible. The tapping process is to be very consistent averaging two taps per second. Three replicates for each sample was conducted. The ratio of bulk and tapped density was used to find Hausner's ratio (HR) and Carr's index (CI) as described in Chapter 2 were calculated for the cornmeal powder based on the following formula:

$$\text{Tapped density} = \frac{W_s}{V_t} \tag{3.5}$$

where W_s is the weight of the sample (kg) and V_t is the volume occupied after tapping (m^3).

$$\text{Hausner's ratio (HR)} = \frac{\text{tapped density}}{\text{bulk density}} \tag{3.6}$$

$$\text{Carr's Index (CI)} = \frac{\text{tapped density-bulk density}}{\text{tapped density}} \times 100\% \tag{3.7}$$

3.3.6. Particle density

The particle density was measured using a helium multipycnometer (Quantachrome MVP 4AC232, FL, USA) which works on the principle of gas displacement. The instrument measured the volume of the cornmeal powder sample based on the following equation:

$$V_p = V_c + V_r\left(\frac{P_1}{P_2} - 1\right) \tag{3.8}$$

where V_p = volume of sample (powder) (m^3), V_C is the volume of the cell (m^3), V_r is the volume of the reference chamber (m^3), P_1 (Pa) represents the pressure in V_r, and P_2 (Pa) is Pressure in V_C and V_r.

Helium is used for determining the average particle volume due to its small size which permits it to occupy pores filled with air and its inert nature makes is suitable for most sample testing. The procedure involves allowing helium which is under pressure to flow from the reference cell into a cell containing a sample of material. This test was repeated three times and the particle density was obtained by taking the ratio of mass of the sample and the average particle volume as

$$\text{Particle density} = \frac{W_s}{V_p} \quad (3.9)$$

where W_s is the mass of the sample (kg) and V_p is the average volume of the particle (m^3).

3.3.7. Porosity

The porosity of the sample at room temperature was determined using the volume of the bulk solid and the volume of the particle using the equation below:

$$\emptyset = \left(\frac{V - V_p}{V}\right) \times 100\ (\%) \quad (3.10)$$

where $\emptyset$ is porosity (%); V is bulk volume of the bulk (m^3); and V_p is particle volume of the bulk (m^3).

3.3.8. Angle of repose

The angle of repose was measured based on ASTM C1444 (ASTM, 2000) standard method by pouring the powder into a funnel which was held at a fixed height above a flat base as described by A. Bodhmage (2006). The funnel outlet was kept at a height of 6 cm above the base as per ISO 3435/1. The sample was poured in the funnel at a constant rate manually until the tip of the powder cone touched the funnel nozzle. The diameter of the cone formed was measured at the base in four places to determine the angle of the cone based on the following formula:

$$\propto = \tan^{-1}\left(\frac{H}{R}\right) \tag{3.11}$$

where H is the height of the cone (m) and R is the mean radius of the cone base (m). Figure 3.2 shows a schematic of the method.

The powder was collected on the flat base and the average of the angle between the horizontal and the slope of the sample on both, left and right sides taken (Emery *et al.*, 2009). This test was repeated three times for each moisture content. This angle corresponds to the flow properties of the powder and is a direct indication of potential flowability.

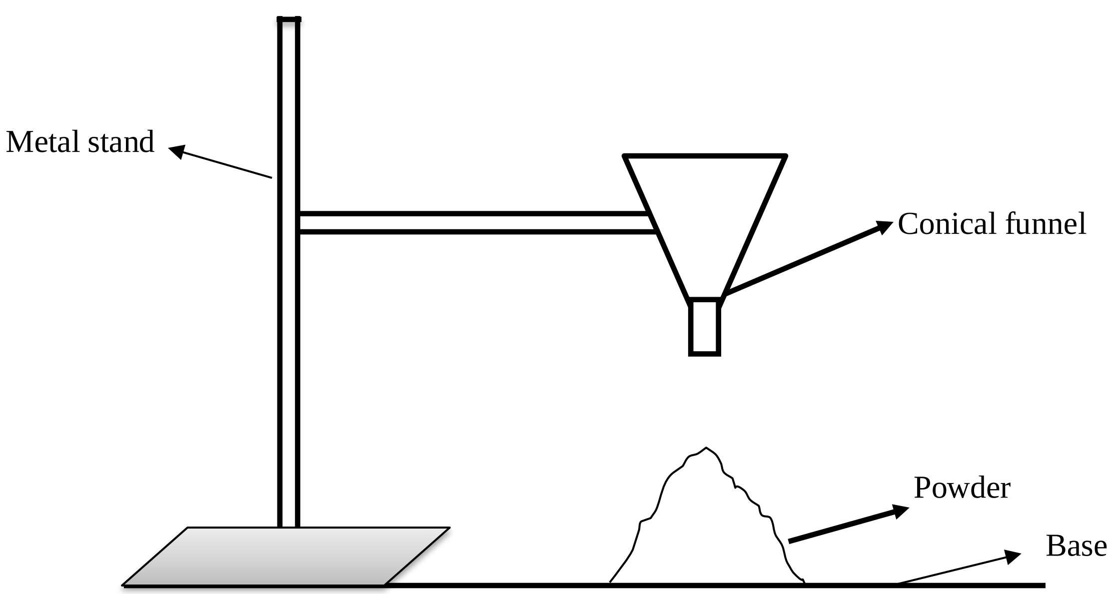

Figure 3.2. Angle of repose measurement schematic

3.3.9. Particle size distribution

Particle size analysis was carried out using a LS 13 320 multi-wave length laser diffraction particle size analyzer (Beckman Coulter Inc., Miami, FL) which uses the theory of Mie scattering, Fraunhofer diffraction and Polarization Intensity Diffraction Scattering (PIDS). The method measures the size distribution of particles suspended in either a liquid or in dry powder form by using the principles of light scattering due to diffraction, reflection, refraction and absorption. The scattering of light depends on the wavelength of the light and on optical properties of the material and is caused when light illuminates a material with a dielectric constant different from that of the surrounding medium (Althaus, 2009b). The instrument measures particle size over the range of 0.017 μm to 2000 μm. The scattering pattern is based on the angle at which the light gets scattered which is characteristic of the particles size. The LS 12 320 uses a 780 nm laser as light source which is accompanied by 126 detectors that measure the intensity of light at varying scattering angles. In this study, approximately 10 g of cornmeal powder was taken in the beaker and analyzed for the particle size distribution. In laser diffraction method, median value (D_{50}) is more frequently reported as compared to mean value. The mean diameter was given by:

$$D[4,3]= \frac{\sum_1^n D^4{}_i}{\sum_1^n D^3{}_i} \qquad (3.12)$$

3.3.10. Flow function

The flowability of the cornmeal powder was measured with an instantaneous flow function (FF) test using the Brookfield Powder Flow Tester (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA) (Figure 3.3) which complies with the ASTM D6128 (ASTM, 2016) – (Standard Test Method for Shear Testing of Bulk Solids Using the Jenike Shear Tester) test procedure using the annular and Jenike's shear test techniques (Xanthakis *et al.*, 2015). The PC connected to the PFT uses Powder Flow Pro V1.2 software to report the data from the tests. The flow function was tested at five uniaxial stresses between 0.3 and 4.8 kPa and three over-consolidation stress levels using a vane lid and running a standard flow function test program. The powder was placed in the trough with volume 263 cm^3 and tested using the powder flow tester. The powder was first critically consolidated under known normal load and then sheared to fail under four normal stresses, less than the consolidation stress. The shear stress at failure was plotted against normal stress at each consolidation stress to construct a best-fit yield locus (Crowley *et al.*, 2014). Five yield loci were created by repeating this process five times. The steady state point, consolidation end point and multiple over consolidation points comprise each yield locus. The flow function curve is plotted between unconfined failure strength and the major principal consolidating stress and is used to characterize the flow based on the region the curve falls into. The value of unconfined yield strength determines how the flow index will be affected on applying a particular value of consolidation yield stress. Powders with good flowability will have a lower value of unconfined yield strength.

$$ff_c = \sigma_1/\sigma_c \tag{3.13}$$

where, σ_1 is the consolidation yield stress (kPa)

σ_c is the unconfined yield strength (kPa)

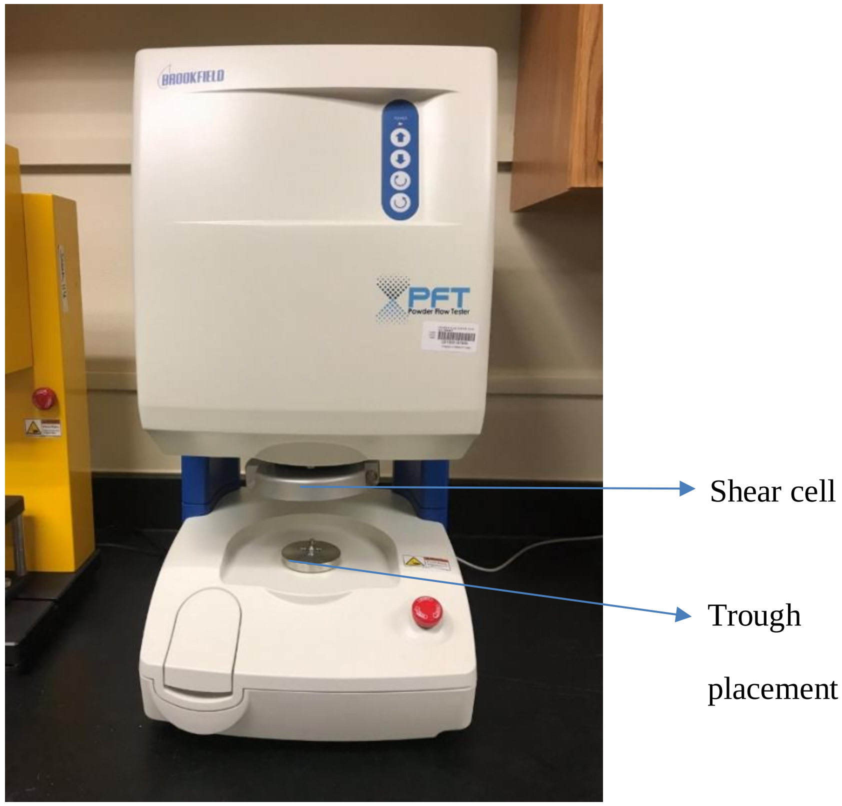

Figure 3.3. Brookfield Powder Flow Tester (PFT3115)

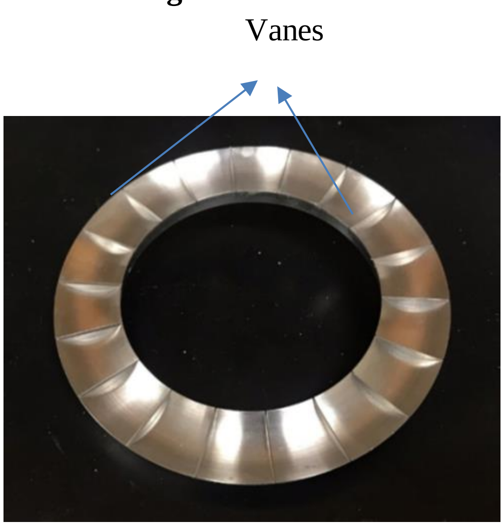

Figure 3.4. Vane lid for flow function test

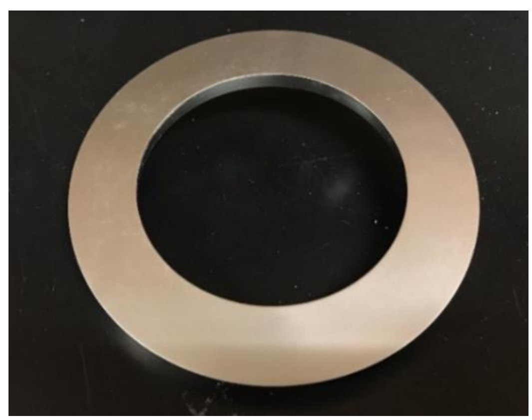

Figure 3.5. Wall friction lid for wall friction test

3.3.11. Angle of internal friction

The flow function test was used to calculate the angle of internal friction using a 23 cm^3 trough. Unconfined failure strength and major principal consolidating stress were calculated from two specific Mohr circles from each yield locus. The effective angle of internal friction was calculated by measuring the angle between the line which begins at the origin and is a tangent to the consolidation Mohr circle, and the normal stress axis. The angle of internal friction can be measured using the flow function test type of Brookfield Powder Flow Tester. The equation representing the angle of internal friction is given below:

$$\tau = \tan\emptyset_i\sigma + C \tag{3.14}$$

Where σ is the shear stress (Pa), $\emptyset_i$ is the angle of internal friction; σ is the normal stress (Pa), and C is the cohesion (Pa).

3.3.12. Angle of wall friction

A flat wall friction lid was used to measure the friction between the powder particles and the wall using a 263 cm^3 trough. A wall yield locus was constructed for the powder being tested based on the maximum shear stress developed between the bulk powder and the wall material under the three normal stresses before the steady-state flow occurs. The wall friction angle was calculated by measuring the shear stress required to move the powder continuously across a stainless-steel surface under three normal stresses, 4.8, 3.2, and 1.6 kPa, applied in order of decreasing normal stress. Angle of wall friction helped understand the effect of moisture on the walls of the container.

$$\emptyset_w = \arctan(\mu) \tag{3.15}$$

where $\emptyset_w$ is the angle of wall friction, and μ is the coefficient of wall friction calculated from the slope of the straight line plotted from the origin and intersecting the maximum wall yield locus at a normal stress value of 4.8 kPa.

3.4. Correlations among the different cornmeal properties

Correlations between the different properties were established using JMP 13 statistical software. Physical properties were compared with each other and expressions for estimating the properties were generated. The data was also used to determine any correlation among the properties. A value of -1 represented a negative linear relationship; a value of 0 represented no linear relationship; and a value of 1 represented a positive linear relationship.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Physical properties of cornmeal samples

4.1.1. Particle density

The moisture content and concentration of calcium stearate have a significant effect on the particle density of the cornmeal powder ($p < 0.05$) (Table 4.1). In all the cases for varying moisture content, the particle density decreased as the moisture content increased. However, at 0.75% (wt/wt) calcium stearate concentration, the particle density did not change significantly ($p<0.05$) when the moisture content increased from 13.5% to 17.0% (w.b.).

The cornmeal powder at 10.0% (w.b.) had the highest density and the property decreased significantly ($p<0.05$) with increasing moisture. This decrease in the particle density as the moisture increased can be attributed to the drastic increase in the volume of cornmeal powder as compared to the mass of the particles. Basically, the volumetric expansion occurs faster than the increase in the mass of the particles (Oginni, 2014).

Higher particle density is a result of reduction of pore spaces within the sample, which results in reduced flowability due to increased compressibility. However, the flowability of cornmeal powder increased with decreasing moisture content (explained in later sections). Therefore, the flowability of cornmeal powder is not just a function of particle density but other factors do have a more prominent effect on flow behavior.

The mean particle density increases with the addition of calcium stearate due to the incorporation of the mineral particles within the sample. The particles of the conditioner, being smaller in size, adhered to the particles of the cornmeal which led to an increase in the particle density. After a certain point, the particles of the conditioner were no longer able to adhere to the particles of the cornmeal and segregated out in the bulk sample leading to a drop in particle density. Overall, the particle density varied from 1258.87 ± 3.53 to 1419.61 ± 4.14 kg/m^3. The values for particle density at 20.0% moisture content (w.b.) are significantly ($p<0.05$) different from the values at other moisture content due to the significant increase in the particle volume. According to Figure. 4.1, there is a sharp decrease in the particle density at all moisture contents as the value for calcium stearate concentration reaches 1.00% wt/wt as the increase in the particle density on addition of calcium stearate is overcome by the increase in the size of the particles since the moisture becomes a dominant factor. The finding is further evaluated in consequent sections by looking at other physical properties.

The relationship between the cornmeal particle density, moisture content (on wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$\rho_p = 1435.54 - 7.87 \times MC(w.b.) + 57.48 \times CS\left(\%\frac{wt}{wt}\right) \quad (4.1a)$$

$$\rho_p = 1419.26 - 5.69 \times MC(d.b.) + 57.48 \times CS\left(\%\frac{wt}{wt}\right) \quad (4.1b)$$

where ρ_p is the particle density (kg/m^3), MC is the moisture content and CS is calcium stearate

Table 4.1. Particle density (kg/m^3) of cornmeal powder as a function of moisture content and calcium stearate concentration at 25°C

MC (w.b.)	Calcium Stearate (wt/wt)			
	0.00 %	**0.50%**	**0.75%**	**1.00%**
10.0%	$_x$1338.86^a ± 10.88	$_y$1397.15^a ± 7.33	$_z$1419.61^a ± 4.14	$_w$1388.50^a ± 5.99
13.5%	$_x$1317.31^b ± 2.21	$_y$1383.66^b ± 1.95	$_y$1390.50^b ±9.63	$_z$1360.43^b ±4.83
17.0%	$_x$1282.13^c ± 9.90	$_y$1364.07^c ± 3.33	$_z$1379.32^b ± 6.96	$_w$1340.82^c ±3.11
20.0%	$_x$1258.87^d ± 3.53	$_y$1335.59^d ± 10.22	$_y$1325.31^c ± 2.41	$_z$1299.18^d ± 5.24

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a-d)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($p < 0.05$).

$^{(x-w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($p< 0.05$).

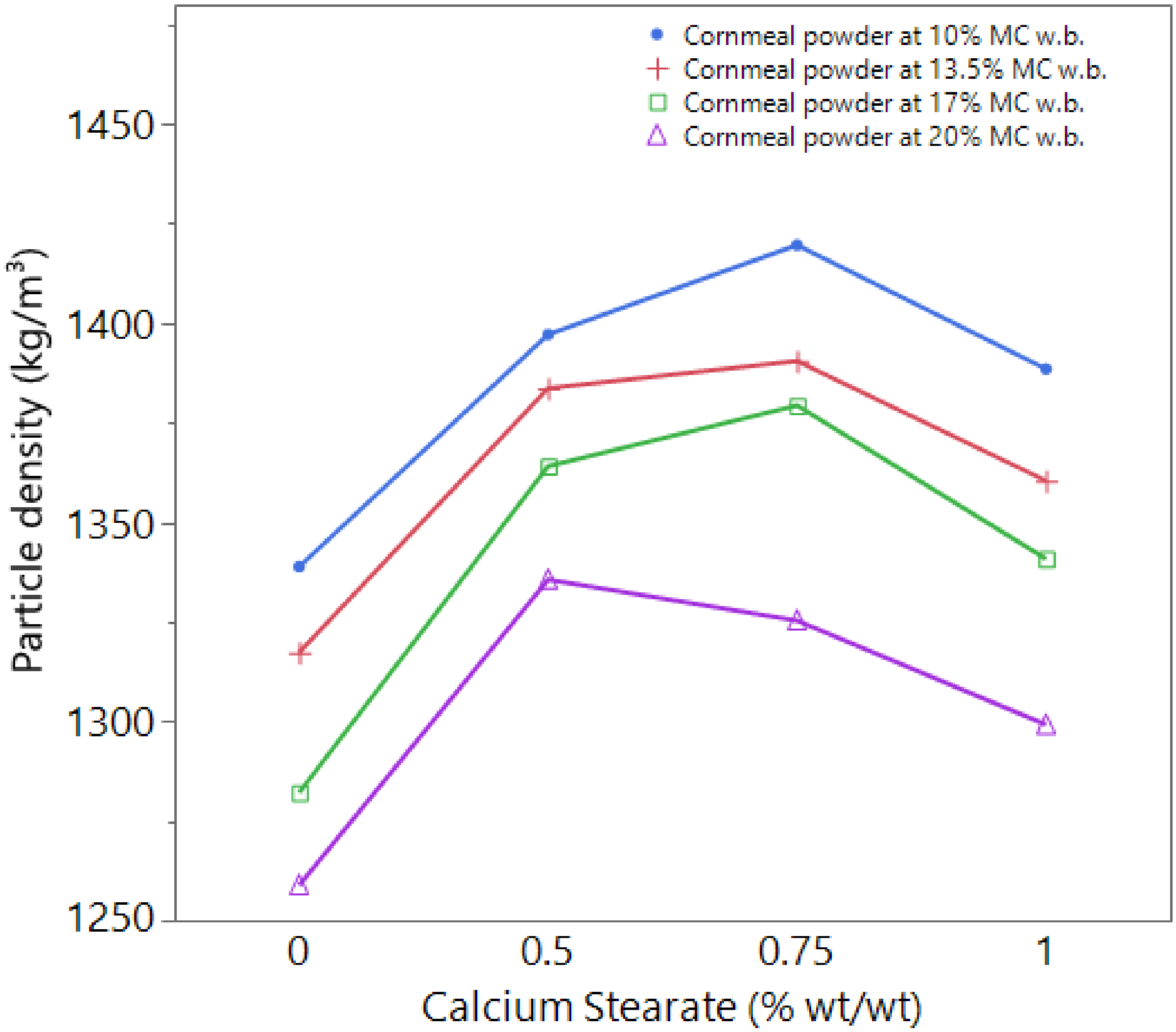

Figure 4.1. Effect of addition of calcium stearate on the particle density of cornmeal powder at varying moisture content at 25°C.

4.1.2. Bulk density

The bulk density of samples with no added calcium stearate decreased from 626.14 ± 7.124 kg/m^3 to 546.96 ± 5.608 kg/m^3 for moisture content varying from 10.0% (w.b.) to 20.0% (w.b.) (Table 4.2). The mean densities were significantly different at the different moisture contents ($p < 0.05$). This significant decrease in the bulk density can be attributed to the absorption of moisture by the particles thereby increasing their particle sizes. Thus, the increase in size (volume) is greater as compared to the mass of the particles which causes the decrease in the bulk density. In case of the cornmeal samples with added conditioner (calcium stearate), the trend was similar with considerably different ($p < 0.05$) mean densities for moisture content varying from 10.0% to 20.0% (w.b.) (Table 4.2). The bulk density increased with the addition of calcium stearate to the cornmeal powder. Peleg *et al.* (1973) noted a similar trend for powdered sucrose on addition of calcium stearate.

The impact of added moisture on the bulk density of biological materials such as wormy compost and soybean grain (Bahram *et al.*, 2013; Kashaninejad *et al.*, 2008; Oginni, 2014) was found to be similar to the effect of moisture on the bulk density of the cornmeal powder evaluated in this study. The volumetric expansion of the bulk sample is greater than the increase in the mass resulting in lower bulk density (Colley *et al.*, 2006). Therefore, the higher the moisture content of the cornmeal powder, the greater the need for storage space due to increase in volume of the bulk.

At 10.0% moisture content (w.b.), the concentration of calcium stearate did not affect the ($p>0.05$) bulk density of the powders (Table 4.2) which suggests that calcium stearate particle impact the bulk almost negligibly at low moisture contents (10.0% w.b.) whereas for higher moisture contents, the impact on bulk density is somewhat significant. Powders with low bulk density have high friction between the particles (Oginni, 2014). For instance, cornmeal powder at 20.0% moisture content (w.b.) will have the highest friction between the particles which will be responsible for potential flow problems such as creating a stable arch at the outlet of the storage silo. The combination of increased friction and cohesion will prevent the powder to flow out from the storage silo. Smaller sized particles therefore have better flowability and the best flow behavior would be exhibited by samples at 10.0% moisture content (w.b.) and calcium stearate concentration in between 0.50% and 1.00% as the mean bulk density is not significantly different ($p<0.05$) for these concentrations of calcium stearate. Samples at moisture content greater than 17.0% (w.b.) would typically be classified at material with poor flow behavior. The relationship of the bulk density with moisture content (both in wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$\rho_b = 666.70 - 5.11 \times MC(w.b.) + 30.93 \times CS\left(\%\frac{wt}{wt}\right) \quad (4.2a)$$

$$\rho_b = 656.26 - 3.69 \times MC(d.b.) + 30.93 \times CS\left(\%\frac{wt}{wt}\right) \quad (4.2b)$$

where ρ_t is bulk density (kg/m^3), MC is the moisture content, and CS is calcium stearate

Table 4.2. Bulk density (kg/m^3) of cornmeal powder at varying moisture content and calcium stearate concentration at 25°C.

MC (w.b.)	Calcium Stearate (wt/wt)			
	0.00%	**0.50%**	**0.75%**	**1.00%**
10.0%	$_{x}$626.14^{a} ± 7.12	$_{x,y}$628±29^{a} ± 4.46	$_{x,y}$633.56^{a} ± 2.01	$_{y}$637.60^{a} ± 4.99
13.5%	$_{x}$610.66^{b} ± 6.05	$_{x,y}$616.70^{b} ± 1.47	$_{y}$621.78^{b} ± 3.75	$_{y}$624.34^{b} ± 7.79
17.0%	$_{x}$573.66^{c} ± 3.33	$_{y}$593.54^{c} ± 5.11	$_{z}$607.91^{c} ± 6.72	$_{z}$614.06^{b} ± 4.62
20.0%	$_{x}$546.96^{d} ± 5.61	$_{y}$581.47^{d} ± 6.07	$_{z}$594.67^{d} ± 1.57	$_{z}$601.95^{c} ± 4.28

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a-d)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($p < 0.05$).

$^{(x-w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($p < 0.05$).

4.1.3. Tapped density

The moisture content and concentration of calcium stearate have a significant effect ($p<0.05$) on the tapped density of cornmeal powder (Table 4.3) Tapped density for the cornmeal powder without the conditioner increased with increasing moisture content. This behavior is explained by the fact that the powder particles when tapped come closer together and start to fill the voids between the particles. In other words, better packing fraction attained by the particles (A. K. Bodhmage, 2006; Oginni, 2014). The samples at higher moisture content had liquid bridging between the particles leading to an increase in bulk volume. This volume was reduced when the samples were subjected to tapping causing the bridges to break. Subjecting cornmeal powder to vibrations during storage, distribution and handling will result in an increase in tapped density values, which may cause flow problems as powders when stored in silos under self-weight will rearrange and cause an increase in density. Similar trends have been reported for other powdered materials such as pharmaceutical powders (Emery *et al.*, 2009; Lam *et al.*, 2008).

The tapped density of samples with no conditioner (no calcium stearate in the cornmeal powder sample) decreased from 695.66 ± 3.76 kg/m^3 to 708.23 ± 5.82 kg/m^3 for moisture content varying from 10.0% (w.b.) to 20.0% (w.b.). The relationship of the tapped density with moisture content (both in wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$\rho_t = 628.55 - 4.32 \times MC(w.b.) + 54.72 \times CS \left(\% \frac{wt}{wt}\right) \qquad (4.3a)$$

$$\rho_t = 637.58 - 3.12 \times MC(d.b.) + 54.72 \times CS \left(\% \frac{wt}{wt}\right) \qquad (4.3b)$$

where ρ_t is tapped density (kg/m^3), MC is the moisture content, and CS is calcium stearate

Cornmeal powder sample with 0.05% calcium stearate at 10.0% moisture content (w.b.) is supposed to have the best flow behavior as it has the least tapped density, meaning that the particles have not rearranged themselves to attain a better packing fraction. The actual flow behavior should be predicted using Hausner's Ratio and Carr's Index as they help in quantifying the flow behavior.

Table 4.3. Tapped density (kg/am^3) of cornmeal powder at varying moisture content and calcium stearate concentration at 25°C.

MC (w.b.)	Calcium Stearate (wt/wt)			
	0.00%	**0.50%**	**0.75%**	**1.00%**
10.0%	$_x695.66^a \pm 3.76$	$_x691.86^a \pm 5.65$	$_y709.73^a \pm 3.58$	$_y716.53^a \pm 3.51$
13.5%	$_x698.73^b \pm 6.14$	$_x699.50^a \pm 2.19$	$_y723.90^b \pm 9.85$	$_z748.86^b \pm 7.10$
17.0%	$_x705.70^c \pm 9.85$	$_x698.46^a \pm 5.01$	$_y745.66^c \pm 5.06$	$_z768.37^c \pm 7.43$
20.0%	$_x708.23^d \pm 5.82$	$_y728.93^b \pm 5.98$	$_y762.10^d \pm 9.01$	$_w792.63^d \pm 4.08$

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a\text{-}d)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($p < 0.05$).

$^{(x\text{-}w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($p< 0.05$).

4.1.4. Hausner's Ratio and Carr's Index

The bulk and tapped density values obtained in sections 4.2 and 4.3 were used to determine the Hausner's Ratio and Carr's Index to relate both densities to the flowability of the powder. The values for HR and CI given in Table 2.1 were used to classify the flow behavior of the cornmeal powders.

For cornmeal powder without conditioner, the values of Hausner's ratio and Carr's Index increased with an increase in moisture content, suggesting a decrease ($p < 0.05$) in the flowability of the powders (Tables 4.4 and 4.5). Since the particles started rearranging and filling the voids, the cornmeal powder attained higher density which gave rise to stronger Van der waal forces between the particles increasing the number of contact points (Mani *et al.*, 2006; Peleg, 1977). This force along with other factors such as increase in forces due to liquid bridging due to increase in moisture content caused a decrease in the flowability (Peleg, 1977). Mechanical interlocking is caused due to vibrations or pressure when the particles reach a mutual orientation in which they get physically bound (Aulton, 2013; Mohsenin, 1970). The p-values for both, HR and CI, were < 0.05 indicating that the means were significantly different at varying moisture contents and fixed concentrations of calcium stearate.

The mean values for HR and CI are lowest at 10.0% moisture content (w.b.) and 0.50% wt/wt calcium stearate (Tables 4.4 and 4.5) but there is no significance difference ($p > 0.05$) in the values of HR and CI between the different concentrations of calcium stearate at 10.0% moisture content (w.b.). This finding suggests that the values of HR and CI lower than 1.11 and 10, respectively, signify excellent flow properties. Fig 4.4 and 4.5 suggest that at 0.50% concentration of calcium stearate there is a dip in the values of HR and CI which indicates improvement in the flow behavior as the calcium stearate particles started filling the spaces between the cornmeal powder particles and acted as a lubricant to improve the flow. Above 0.50% (wt/wt) calcium stearate concentration, the impact of on the Hausner's Ratio and Carr's Index was reversed as the particle size started dominating the flow behavior. The increase in HR and CI with increasing moisture content is also reported by Chang *et al.* (1998) on a study on different model food powders. The values for Hausner's Ratio and Carr's Index were maximum for samples at moisture content 20.0% (w.b.) due to the increase in the tapped density as seen in Table 4.3. The relationship of Hausner's Ratio with moisture content (in both wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$HR=0.92+0.02\times MC(w.b.)+0.03\times CS\left(\%\frac{wt}{wt}\right) \quad (4.4a)$$

$$HR=0.96+0.01\times MC(d.b.)+0.03\times CS\left(\%\frac{wt}{wt}\right) \quad (4.4b)$$

where HR is Hausner's Ratio, MC is the moisture content and CS is calcium stearate

The relationship of Carr's Index with moisture content (in both wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$CI=-3.14+1.20\times MC(w.b.)+1.87\times CS\left(\%\frac{wt}{wt}\right) \quad (4.5a)$$

$$CI=-0.61+0.87\times MC(d.b.)+1.87\times CS\left(\%\frac{wt}{wt}\right) \quad (4.5b)$$

where CI is Carr's Index, MC is the moisture content, and CS is calcium stearate

Table 4.4. Hausner's Ratio of cornmeal powder at varying moisture content and calcium stearate concentration at 25°C.

MC (w.b.)	Calcium Stearate (wt/wt)			
	0.00%	**0.50%**	**0.75%**	**1.00%**
10.0%	$_{x}1.11^{a} \pm 0.01$	$_{x}1.10^{a} \pm 0.02$	$_{x}1.12^{a} \pm 0.01$	$_{x}1.13^{a} \pm 0.01$
13.5%	$_{x}1.14^{b} \pm 0.02$	$_{x,y}1.13^{b} \pm 0.01$	$_{y}1.16^{b} \pm 0.02$	$_{z}1.20^{b} \pm 0.01$
17.0%	$_{x}1.23^{c} \pm 0.01$	$_{y}1.17^{c} \pm 0.01$	$_{y}1.22^{c} \pm 0.01$	$_{z}1.25^{c} \pm 0.01$
20.0%	$_{x}1.29^{d} \pm 0.02$	$_{y}1.25^{d} \pm 0.01$	$_{y,z}1.28^{d} \pm 0.01$	$_{z}1.31^{d} \pm 0.02$

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a-d)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($p < 0.05$).

$^{(x-w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($p < 0.05$).

Table 4.5. Carr's Index of cornmeal powder at varying moisture content and calcium stearate concentration at 25°C.

MC (w.b.)	Calcium Stearate (wt/wt)			
	0.00%	**0.50%**	**0.75%**	**1.00%**
10.0%	$_{a}9.99^{a} \pm 0.98$	$_{a,b}9.18^{a} \pm 1.25$	$_{a,b}10.73^{a} \pm 0.60$	$_{b}11.01^{a} \pm 0.65$
13.5%	$_{x}12.59^{b} \pm 1.62$	$_{x,y}11.84^{b} \pm 0.31$	$_{y}14.09^{b} \pm 1.38$	$_{z}16.62^{b} \pm 0.86$
17.0%	$_{x}18.70^{c} \pm 0.73$	$_{y}15.02^{c} \pm 0.25$	$_{y}18.47^{c} \pm 0.35$	$_{z}20.08^{c} \pm 0.61$
20.0%	$_{x}22.76^{d} \pm 0.69$	$_{y}20.23^{d} \pm 0.46$	$_{y,z}21.96^{d} \pm 0.73$	$_{z}24.05^{d} \pm 0.85$

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a-d)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($p < 0.05$).

$^{(x-w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($p < 0.05$).

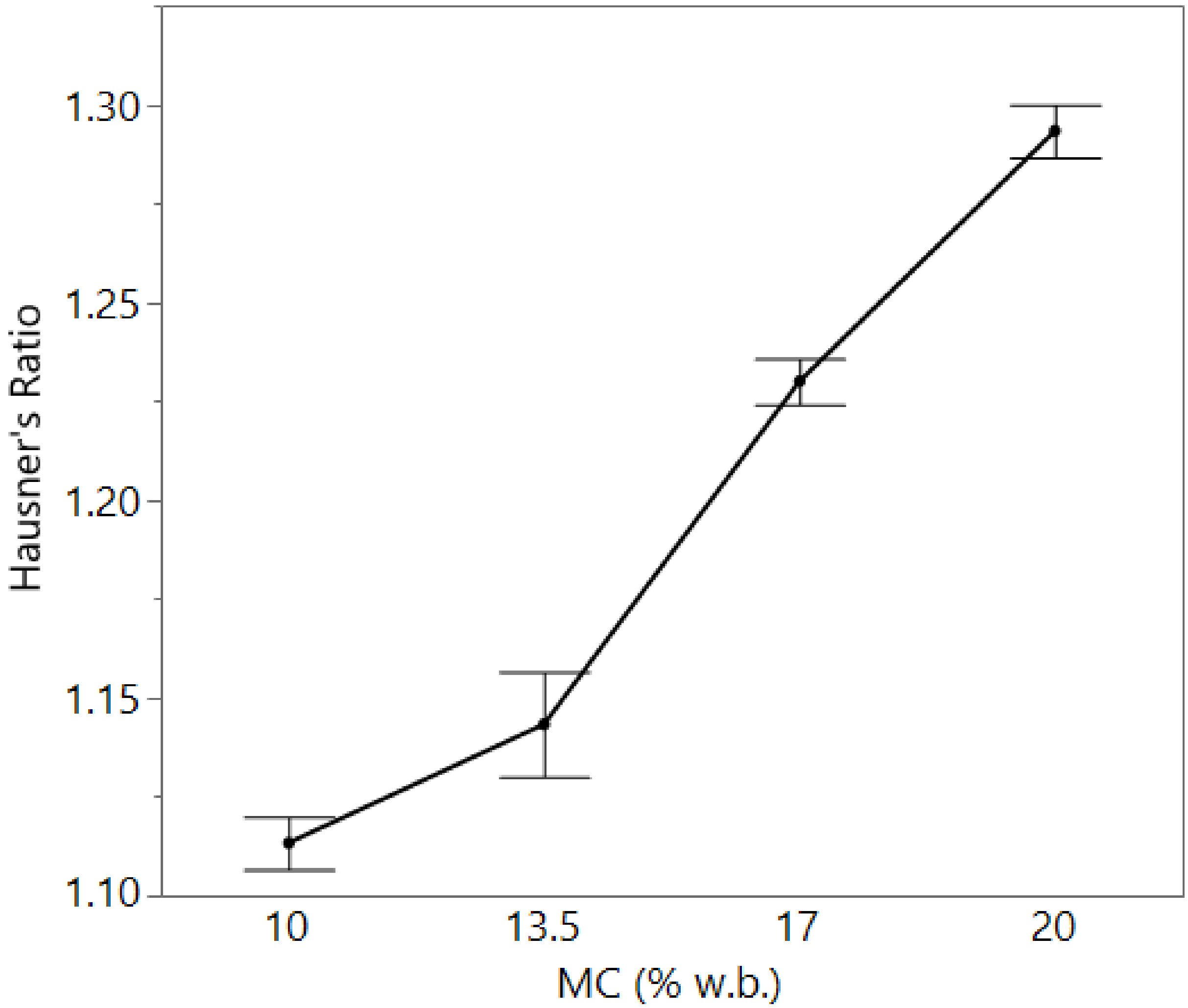

Figure 4.2. Effect of moisture content (% w.b.) on the Hausner's Ratio of cornmeal powder without conditioner at 25°C.

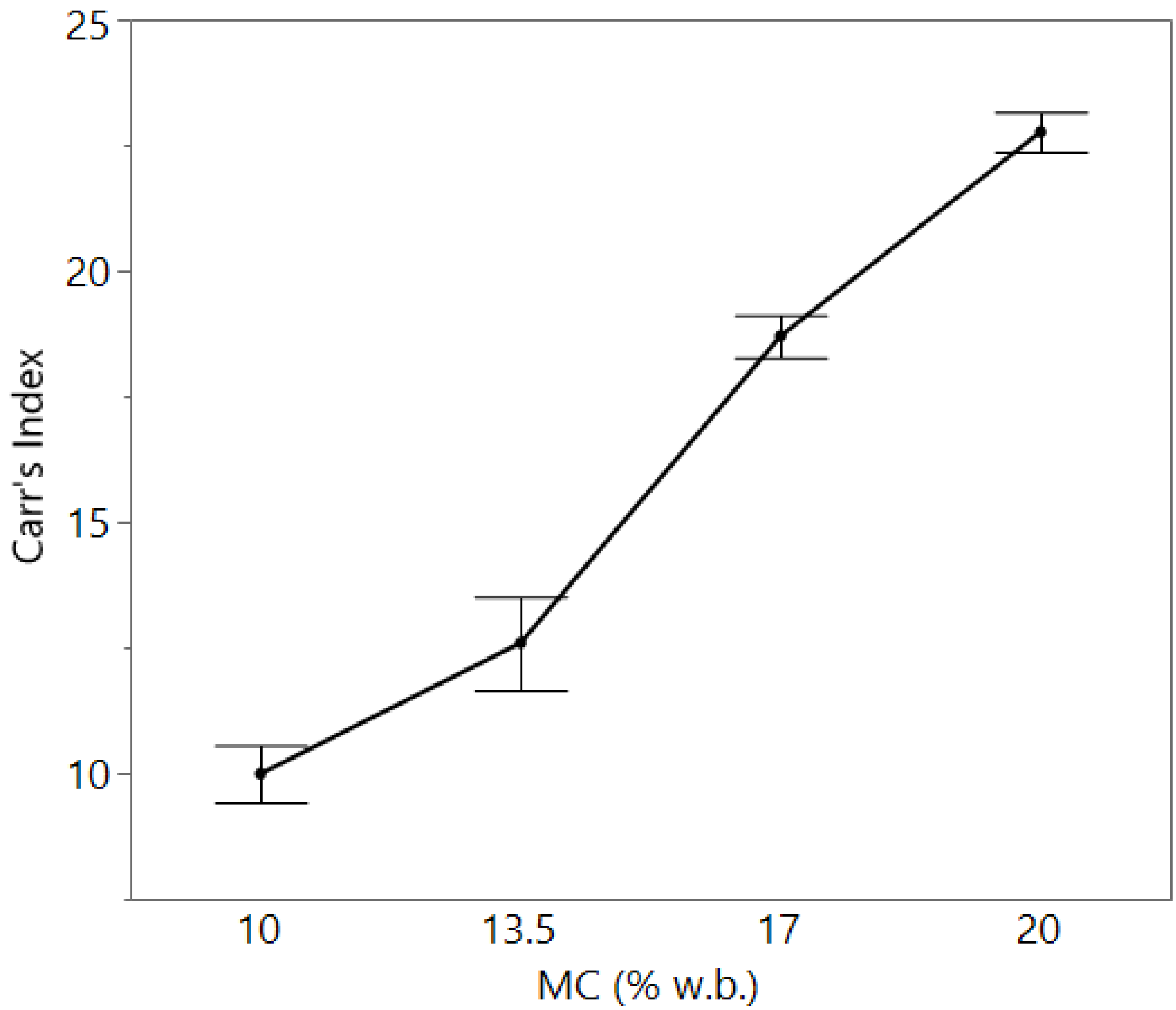

Figure 4.3. Effect of moisture content (% w.b.) on the Carr's Index of cornmeal powder without conditioner at 25°C.

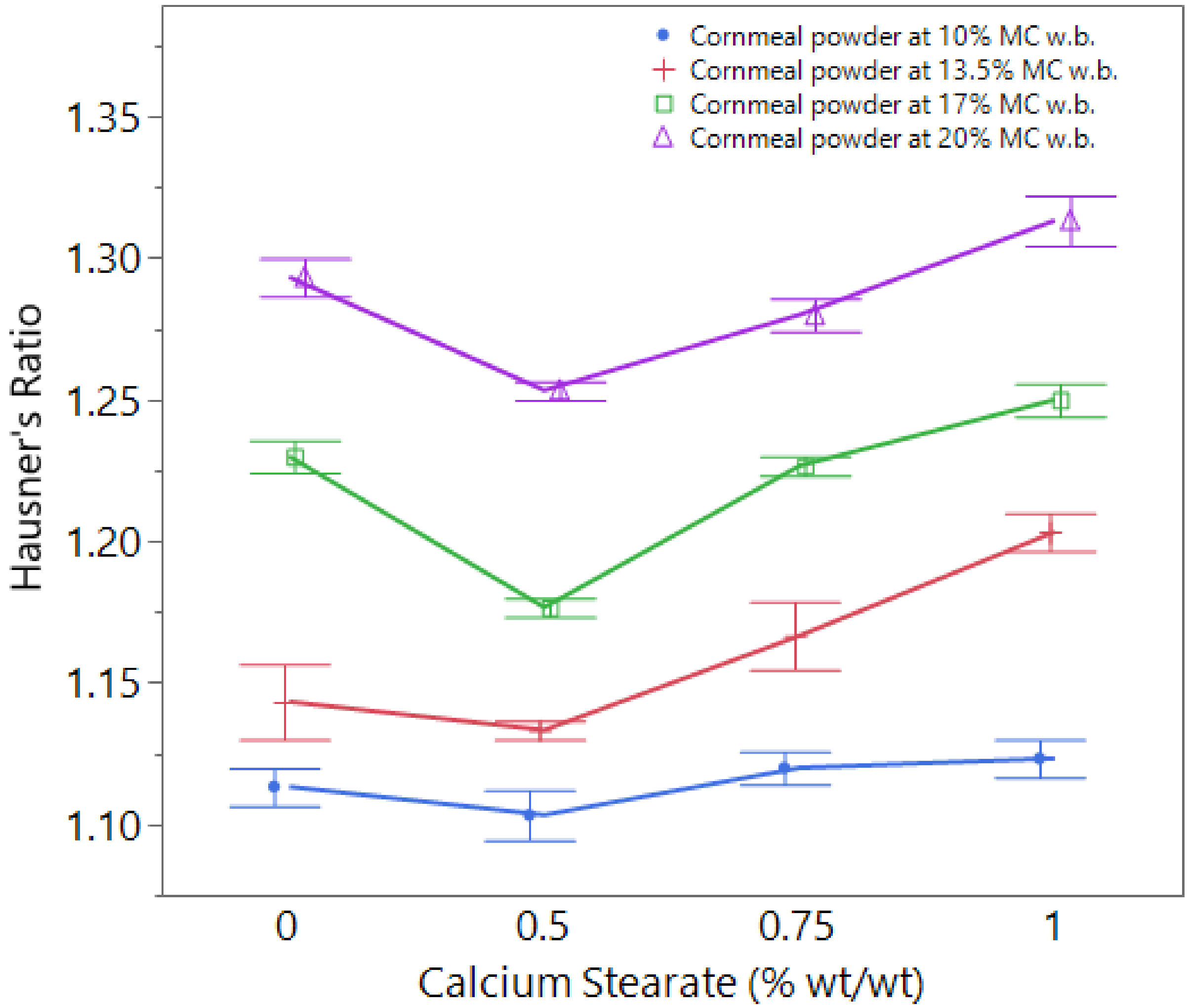

Figure 4.4. Effect of calcium stearate on the Hausner's Ratio of cornmeal powder at varying moisture content at 25°C.

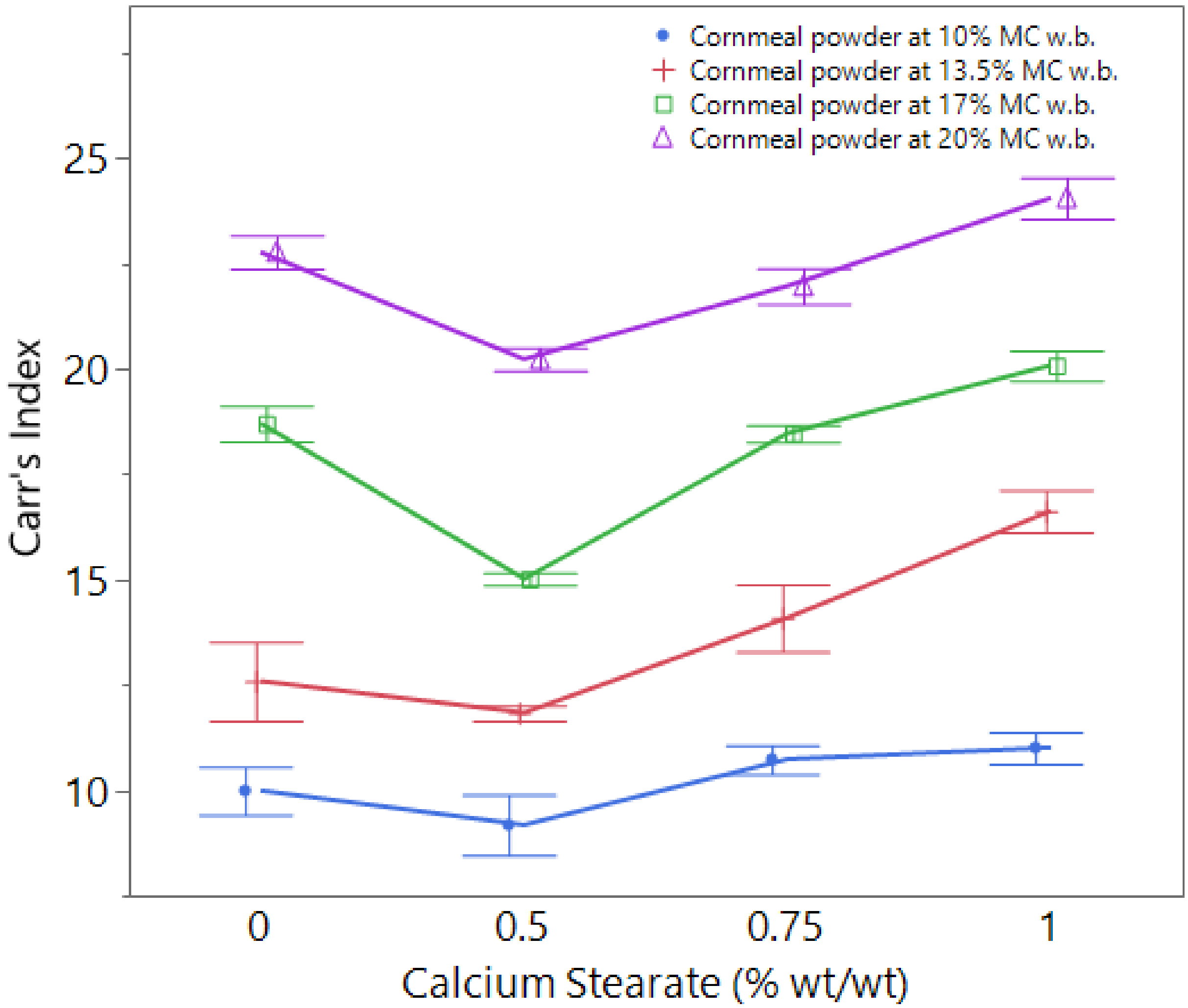

Figure 4.5. Effect of calcium stearate on the Carr's Index of cornmeal powder at varying moisture content at 25°C.

4.1.5. Porosity

Porosity of cornmeal powder increased significantly ($p<0.05$) with increasing moisture content at 0% concentration of calcium stearate (Table 4.6). Particles with an average porosity of 40% are said to be spheroidal in shape (Woodcock *et al.*, 2012). A higher porosity value refers to irregular shaped or small particles.

The porosity of cornmeal powder ranged between 53.25% and 56.62%, indicating that the particles are irregular in shape. The porosity of the samples generally increased with an increase in moisture content. However, at 1.00% wt/wt calcium stearate, the porosity decreased significantly ($p<0.05$) at 20.0% moisture content (w.b.). Bahram *et al.* (2013) noticed a similar trend of reduction in porosity with increasing moisture content for wormy compost. Porosity is given by the difference between particle density and bulk density divided by the particle density. In case of the samples at 1.00% calcium stearate concentration and 20.0% moisture content (w.b.), the difference between particle density and bulk density was smaller as compared to other moisture contents since the particle density was significantly affect by the presence of calcium stearate, and high moisture content lead to drastic decrease in the particle density.

A material such as ground pine, which is highly compressible, has a high value of porosity i.e. 80% (Oginni, 2014). This compressibility is directly related to flow problems. Samples with low bulk density have more occluded air within the powder (Koç *et al.*, 2014). The porosity of the samples increased with an increase in the moisture content due to the increase in the overall size of the particles creating an increase in the number of voids. Sjollema (1963) noted that as the bulk density decreases, porosity increases. The relationship of porosity with moisture content (in both wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$\emptyset=53.44+0.12\times MC(w.b.)-0.41\times CS\left(\%\frac{wt}{wt}\right) \quad (4.6a)$$

$$\emptyset=53.69+0.08\times MC(d.b.)-0.41\times CS\left(\%\frac{wt}{wt}\right) \quad (4.6b)$$

where Ø is the porosity (%), MC is the moisture content and CS is calcium stearate

Table 4.6. Porosity (%) of cornmeal powder at varying moisture content and calcium stearate concentration at 25°C

MC (w.b.)	Calcium Stearate (wt/wt)			
	0.00%	**0.50%**	**0.75%**	**1.00%**
10.0%	$_{x}53.24^{a} \pm 0.38$	$_{y}55.05^{a} \pm 0.23$	$_{y}55.41^{a} \pm 0.13$	$_{z}54.12^{a} \pm 0.20$
13.5%	$_{x}53.69^{a} \pm 0.08$	$_{y}55.48^{b} \pm 0.06$	$_{y}55.33^{a} \pm 0.31$	$_{z}54.13^{a} \pm 0.16$
17.0%	$_{x}55.30^{b} \pm 0.34$	$_{y}56.52^{c} \pm 0.11$	$_{z}55.99^{b} \pm 0.22$	$_{w}54.20^{a} \pm 0.11$
20.0%	$_{x}56.62^{c} \pm 0.12$	$_{x}56.49^{c} \pm 0.33$	$_{y}55.18^{a} \pm 0.05$	$_{z}53.73^{b} \pm 0.19$

The data is represented as: Mean ± SD. Values are means of 3 replications.

(a-d) Means within a column, which are not followed by a common superscript letter, are significantly different ($p<0.05$).

(x-w) Means within a row, which are not followed by a common subscript letter, are significantly different ($p<0.05$).

4.1.6. Angle of repose

The values of the angle of repose at fixed moisture content but varying concentrations of calcium stearate were not significantly different (P>0.05) for all concentrations of calcium stearate (0% to 1.00% wt/wt) (Table 4.7). For instance, at 10.0% moisture, the angles of repose at the lowest tested calcium stearate concentration (i.e. 0% wt/wt) and the highest tested calcium stearate concentration (i.e. 1.00% wt/wt) were 37.00 ± 0.22 and 37.26 ± 0.11 degrees, which depict a small change in value (p>0.05). However, at a fixed concentration of calcium stearate, the angle of repose differed significantly (p<0.05) with the increase in moisture content due to cohesion between the particles.

In general, the more free-flowing powders tend to possess smaller drained angles of repose. Based on the classification mentioned in section 2.4 for flowability using angle of repose values, all the samples exhibited a little amount of cohesiveness i.e. angle of repose ranged between 30 - 45° but mostly exhibited good flow. It is worth noticing that, despite being an easy method to classify flow behavior, measurement of angle of repose yielded very variable results each time and it should not be used for characterization of cornmeal powder flow properties.

The angle of repose was lowest at 10.0% moisture content (w.b.) for all concentrations of calcium stearate. This trend was in accordance with Hausner's Ratio and Carr's Index as they were also the lowest at the same conditions. The most unfavorable situation was at 20.0% moisture content because at each concentration of calcium stearate, the value of angle of repose was highest. The relationship of the angle of repose with moisture content (in both wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$\propto = 32.90 + 0.42 \times MC(w.b.) + 0.12 \times CS\left(\%\frac{wt}{wt}\right) \tag{4.7a}$$

$$\propto = 33.77 + 0.30 \times MC(d.b.) + 0.12 \times CS\left(\% \frac{wt}{wt}\right) \qquad (4.7b)$$

where $\propto$ is the angle of repose (°), MC is the moisture content and CS is calcium stearate

Table 4.7. Angle of repose (degrees) of cornmeal powder at varying moisture content and calcium stearate concentration at 25°C.

MC (w.b.)	Calcium Stearate (wt/wt)			
	0.00%	**0.50%**	**0.75%**	**1.00%**
10.0%	$_{x}37.00^{a} \pm 0.22$	$_{x}37.06^{a} \pm 0.30$	$_{x}37.19^{a} \pm 0.23$	$_{x}37.26^{a} \pm 0.11$
13.5%	$_{x}38.84^{b} \pm 0.54$	$_{x}39.20^{b} \pm 0.95$	$_{x}38.83^{b} \pm 0.32$	$_{x}38.76^{b} \pm 0.42$
17.0%	$_{x}39.40^{b} \pm 0.21$	$_{x}39.19^{b} \pm 0.57$	$_{x}39.77^{c} \pm 0.46$	$_{x}39.48^{c} \pm 0.33$
20.0%	$_{x}41.53^{c} \pm 0.14$	$_{x}41.69^{c} \pm 0.42$	$_{x}41.61^{d} \pm 0.14$	$_{x}41.69^{d} \pm 0.42$

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a\text{-}d)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($p<0.05$).

$^{(x\text{-}w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($p<0.05$).

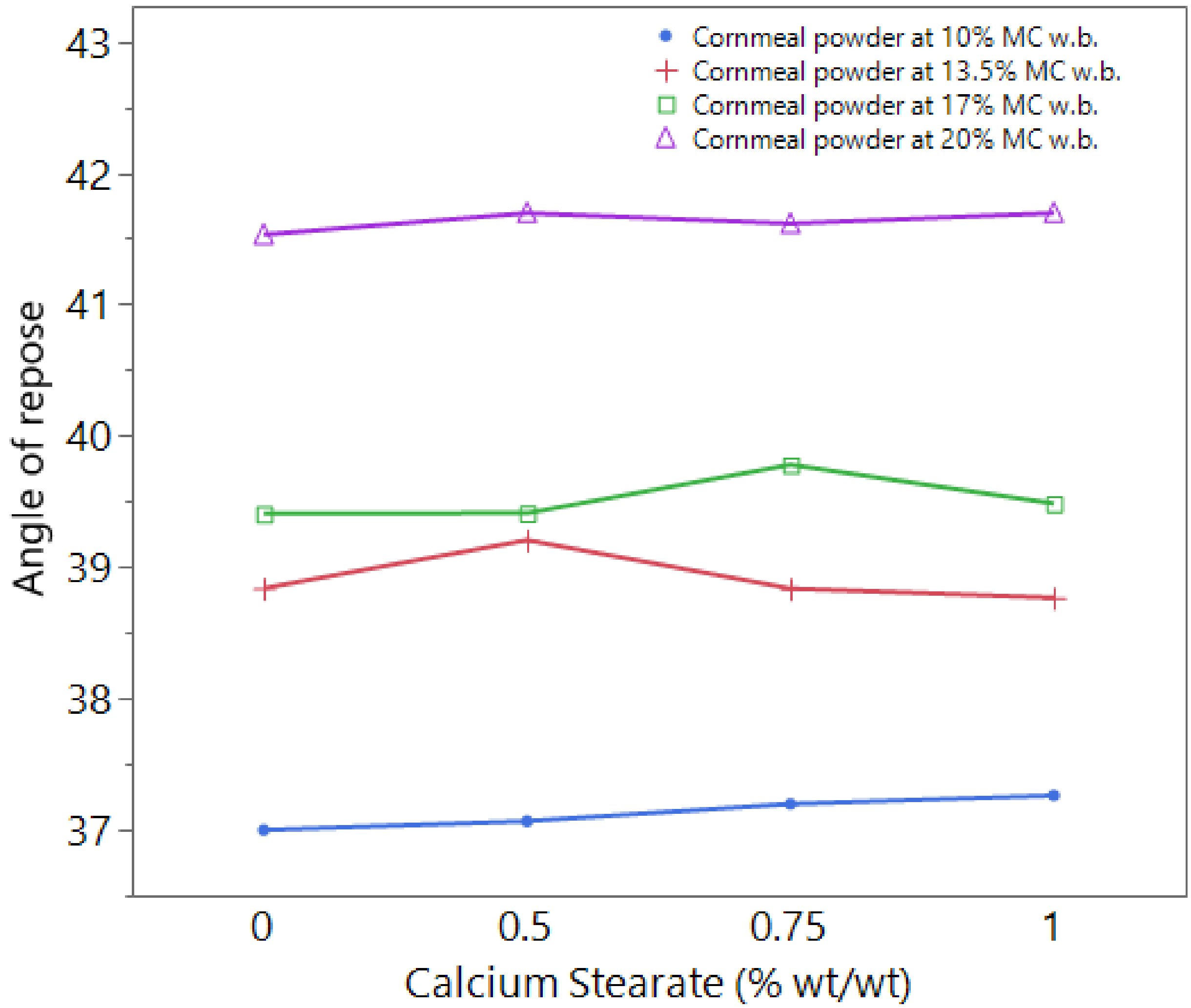

Figure 4.6. Effect of calcium stearate on the angle of repose of cornmeal powder at varying moisture content at 25°C.

4.1.7. Particle size distribution

Mean particle size varied from 567.2 µm to 629.2 µm with moisture content and concentration of calcium stearate in the samples (Tables 4.8 to 4.11, Figures 4.7 to 4.10). The distribution of the particles at different moisture contents showed a similar pattern (Figure 4.7). The particle size distribution does not have any noticeable difference at varying moisture content values without the addition of a calcium stearate. Whereas, for varying moisture content values without the addition of a calcium stearate, the mean particle size differs significantly for the cornmeal powder. It has been previously observed that particles with narrow particle size distribution have better flow characteristics than powders with wider particle size distribution (Benkovic & Bauman, 2009). Figures 4.7 to 4.10 show that the distribution is mostly narrow for varying moisture contents indicating no major issues with flowability. However, particle size cannot be considered the only factor influencing flowability of cornmeal powder.

At fixed concentrations of calcium stearate, the mean particle size was significantly different for samples at varying levels of moisture ($p<0.05$) (Tables 4.8 to 4.11). However, the particle diameter vs. volume plots did not show a marked difference in particle size as a function of moisture content (Figure 4.7 to 4.10). The mean size of cornmeal powder increased with increasing moisture content which can be attributed to the same reason as for the particle density. The volumetric expansion of the particles increased with increasing moisture content.

The particle size distribution for 0% calcium stearate at varying moisture content clearly shows that there is not much difference between the particle size distribution (Figure 4.7) of cornmeal powder even though the mean particle size is significantly different meaning that there are very few particles that are affecting the mean particle size without affecting the distribution.

The mean particle size decreased at fixed moisture content and varying concentration of calcium stearate except at 0.50% wt/wt calcium stearate. The particle size increased from 0% to 0.50% and decreased thereafter. Smaller particles have reduced flowability because of the increase in surface area per unit mass of the powder which increases the frictional forces that aid in resisting the flow (Shenoy *et al.*, 2015). The cornmeal powder at 0.50% wt/wt calcium stearate exhibited better flow behavior as compared to other concentrations of calcium stearate due to the increase in the size of the particles that reduced the fiction between the particles. The relationship of the mean particle size with moisture content (in both wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$D=567.24+2.54\times MC(w.b.)-17.97\times CS\left(\%\frac{wt}{wt}\right) \tag{4.8a}$$

$$D=572.56+1.84\times MC(d.b.)-17.97\times CS\left(\%\frac{wt}{wt}\right) \tag{4.8b}$$

where D is the mean diameter (μm), MC is the moisture content and CS is calcium stearate

Table 4.8. Mean particle size (µm) of cornmeal powder without conditioner at 25°C

MC (w.b.)	Mean (µm)	S.D. (µm)	Volume < 10% (µm)	Volume < 50% (µm)	Volume < 90% (µm)
10.0%	592.5	254.2	248.1	605.7	922.2
13.5%	590.2	275.5	210.0	597.0	943.4
17.0%	600.2	257.6	243.5	614.4	935.4
20.0%	610.2	255.4	259.8	623.9	942.0

Values are means of 3 replications.

SD: Standard deviation

Table 4.9. Mean particle size (µm) of cornmeal powder with 0.50% wt/wt calcium stearate at 25°C

MC (w.b.)	Mean (µm)	S.D. (µm)	Volume < 10% (µm)	Volume < 50% (µm)	Volume < 90% (µm)
10.0%	597.5	242.0	280.7	420.5	609.4
13.5%	605.3	240.1	288.7	617.0	914.9
17.0%	619.8	239.4	307.3	631.2	929.8
20.0%	629.2	242.0	314.3	637.0	941.1

Values are means of 3 replications.

SD: Standard deviation

Table 4.10. Mean particle size (μm) of cornmeal powder with 0.75% wt/wt calcium stearate at 25°C

MC (w.b.)	Mean (μm)	S.D. (μm)	Volume < 10% (μm)	Volume < 50% (μm)	Volume < 90% (μm)
10.0%	575.5	262.2	202.1	590.8	914.5
13.5%	589.1	257.5	232.3	602.9	923.8
17.0%	588.0	247.9	251.7	595.9	914.6
20.0%	606.0	244.7	307.8	597.2	930.4

Values are means of 3 replications.

SD: Standard deviation

Table 4.11. Mean particle size (μm) of cornmeal powder with 1.00% wt/wt calcium stearate at 25°C

MC (w.b.)	Mean (μm)	S.D. (μm)	Volume < 10% (μm)	Volume < 50% (μm)	Volume < 90% (μm)
10.0%	567.2	256.4	208.9	578.1	901.6
13.5%	581.3	245.0	251.7	590.0	900.9
17.0%	585.7	259.9	222.6	597.3	926.3
20.0%	592.2	250.0	250.3	600.6	921.5

Values are means of 3 replications.

SD: Standard deviation

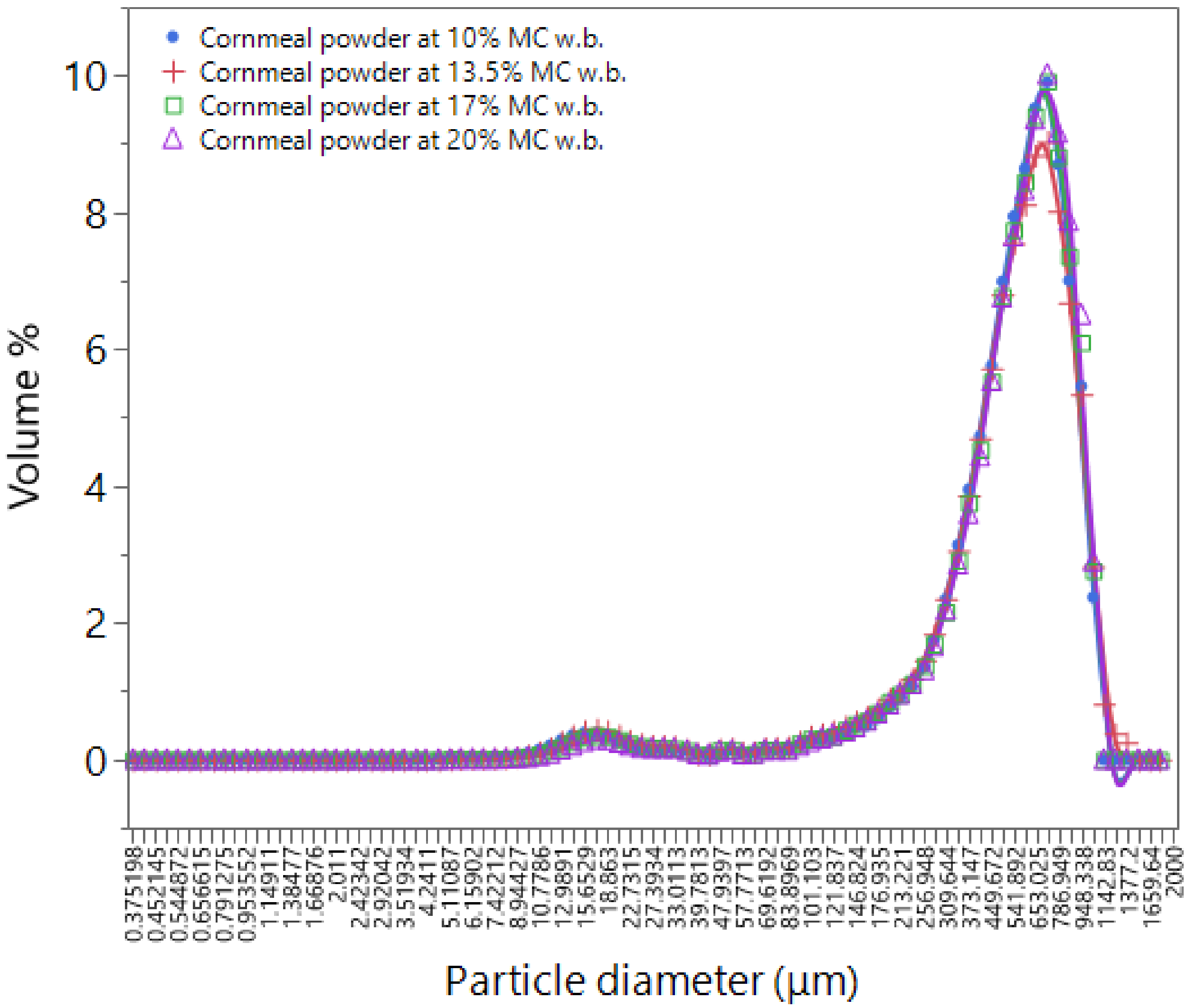

Figure 4.7. Particle size distribution of cornmeal powder with no conditioner at varying moisture content at 25°C.

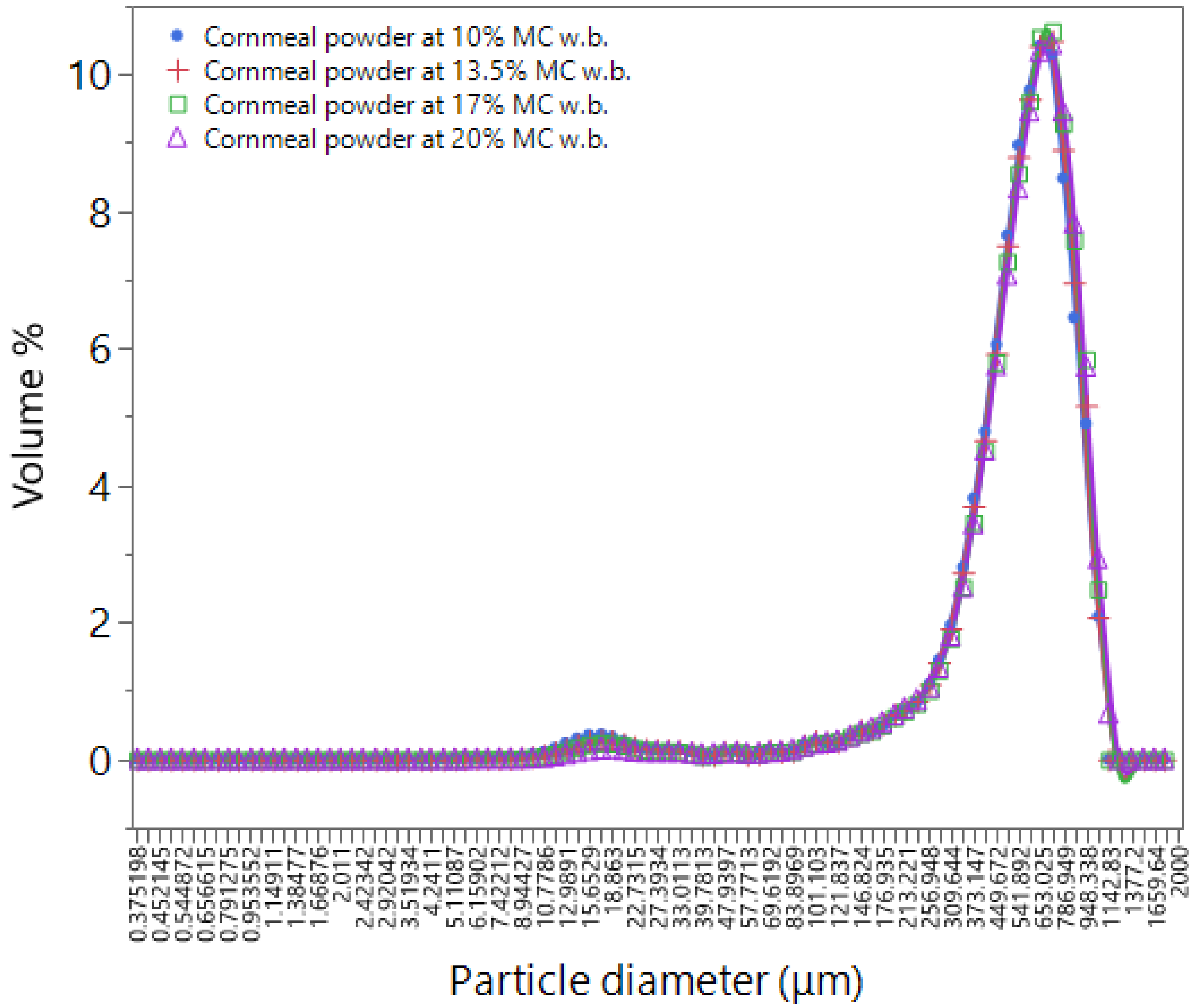

Figure 4.8. Effect of calcium stearate (0.50% wt/wt) on particle size distribution of cornmeal powder at varying moisture content at 25°C.

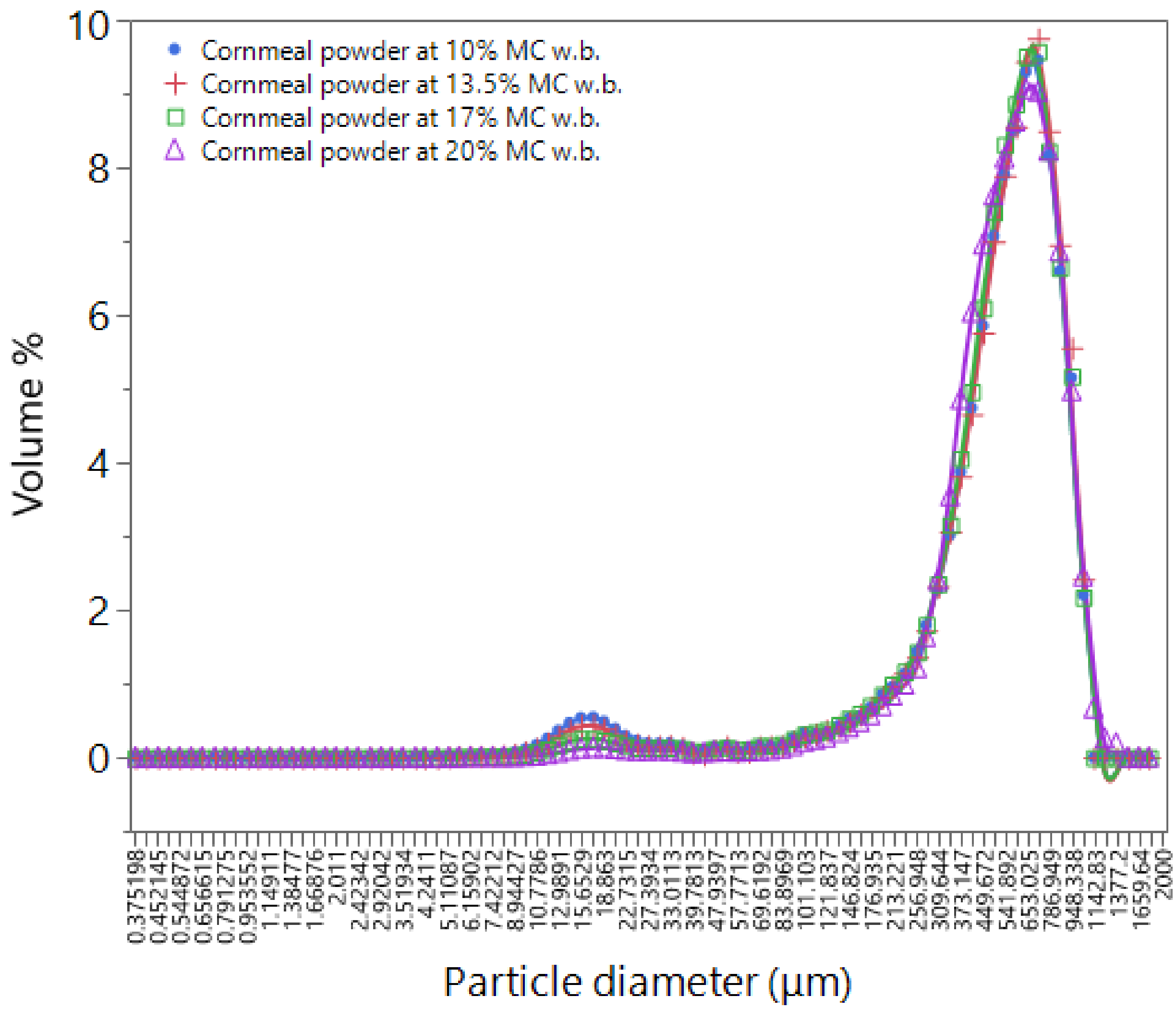

Figure 4.9. Effect of calcium stearate (0.75% wt/wt) on particle size distribution of cornmeal powder at varying moisture content at 25°C.

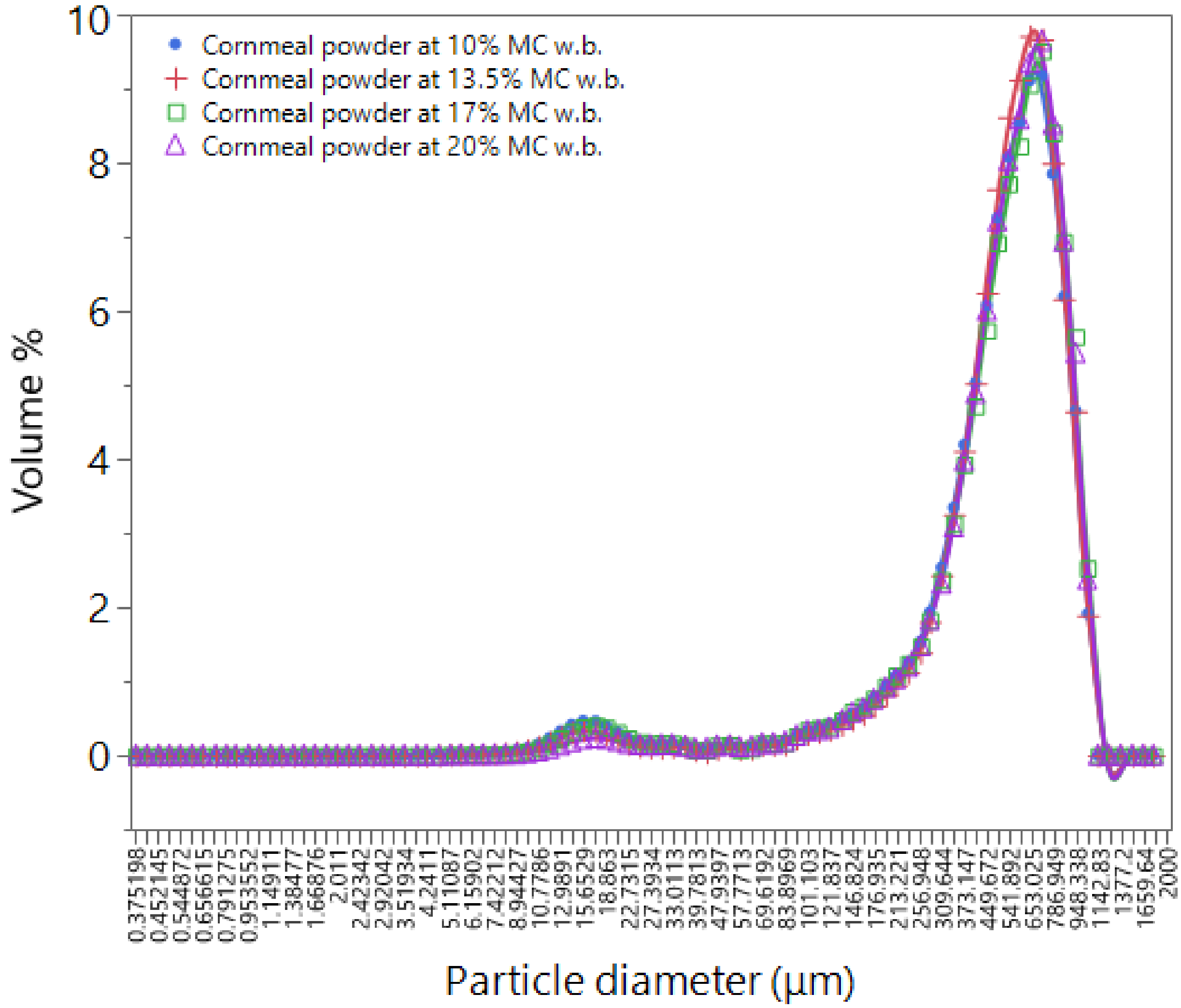

Figure 4.10. Effect of calcium stearate (1.00% wt/wt) on particle size distribution of cornmeal powder at varying moisture content at 25°C.

4.1.8. Moisture isotherms of cornmeal powder

Table 4.12 shows the equilibrium moisture content of the cornmeal powder samples tested at varying relative humilities at 25°C. The samples placed in high relative humidity conditions (above 90% RH) showed mold grow at the end of the fifth day of the experiment. However, samples kept in desiccators with RH less than 80% were free of mold even after 8 days of the experiment. Cornmeal powder samples that were kept at RH<80% at varying concentration of calcium stearate reached equilibrium within 4 days and were tested for moisture content at the end of the fourth day of the experiment. Caking was experienced in the samples kept in desiccators containing potassium sulphate solution after day 5 along with mold growth initiation. The temperature was kept at 25°C as most of the materials are handled at that temperature and attaining it in the incubator was easier.

All the samples followed Type 2 sigmoid isotherms (Figure 4.11). In general, the equilibrium moisture content vs. water activity curve shows an asymptotic trend as the water activity tends towards unity. At water activity values below 0.7, the rate of moisture absorption, represented by the equilibrium moisture content, is slower compared to the rate of absorption at higher water activity values.

The moisture isotherms are usually divided into three regions. Region I ranged between 0 and 0.12 a_w, representing water that exists as a monolayer that is tightly bound to ionic groups such as anions and carboxyl groups (references). Region II ranged between 0.12 and 0.75 a_w representing the multi-molecular moisture, which is less firmly bound than the water in Region I, and Region III ranged between 0.75 and 1.0 $a_{w,}$ in which the moisture exists as free water which is easier to remove (Labuza, 1984). Moisture isotherms of samples with calcium stearate investigated in this study did not (p>0.05) affect the EMC at the given temperature (Table 4.12).

Table 4.12. Equilibrium moisture content (% d.b.) of cornmeal samples at different calcium stearate concentration at 25°C.

Saturated salt solution	A_w	Calcium Stearate (wt/wt)			
		0.00%	0.50%	0.75%	1.00%
LiCl	0.1130	$_x5.19^a \pm 0.01$	$_y4.59^a \pm 0.04$	$_z5.83^a \pm 0.01$	$_z5.79^a \pm 0.02$
$MgCl_2$	0.3278	$_x9.29^b \pm 0.02$	$_y8.97^b \pm 0.02$	$_z9.66^b \pm 0.02$	$_w9.82^b \pm 0.02$
K_2CO_3	0.4316	$_x10.27^c \pm 0.01$	$_y10.65^c \pm 0.01$	$_y10.72^c \pm 0.02$	$_z10.57^c \pm 0.07$
NaBr	0.5760	$_x12.55^d \pm 0.03$	$_x12.31^d \pm 0.16$	$_y13.26^d \pm 0.11$	$_y13.31^d \pm 0.18$
NaCl	0.7529	$_{x,y}16.71^e \pm 0.02$	$_z16.06^e \pm 0.05$	$_y16.62^e \pm 0.03$	$_x16.77^e \pm 0.09$
KCl	0.8434	$_x19.60^f \pm 0.10$	$_x19.64^f \pm 0.02$	$_x19.69^f \pm 0.03$	$_x19.65^f \pm 0.05$
K_2SO_4	0.9730	$_x31.58^g \pm 0.02$	$_y30.48^g \pm 0.05$	$_z32.63^g \pm 0.06$	$_z32.71^g \pm 0.12$

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a\text{-}g)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($p < 0.05$).

$^{(x\text{-}w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($p< 0.05$).

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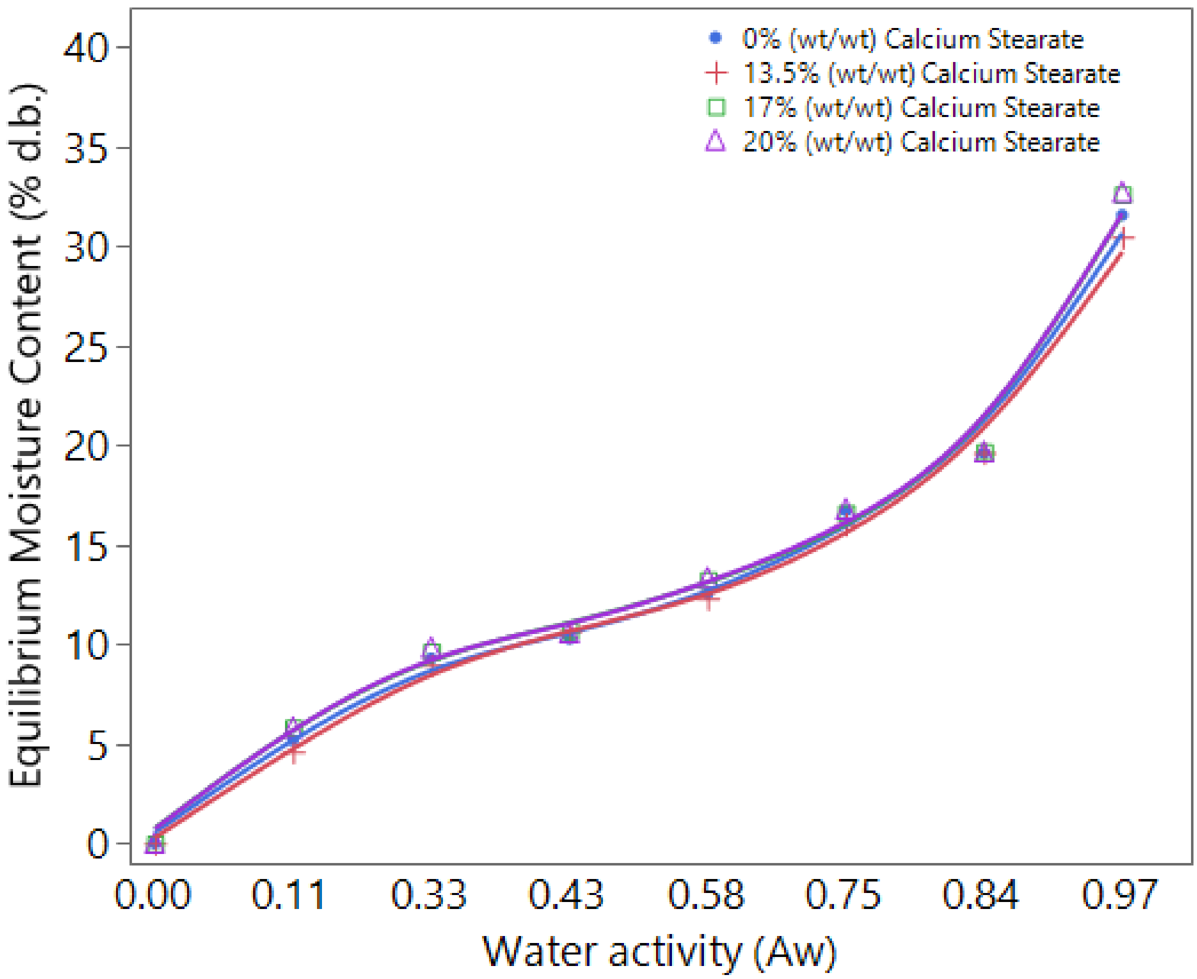


Figure 4.11. Moisture isotherm for cornmeal powder at varying concentration of calcium stearate (wt/wt) at 25°C.

The relationship between EMC and Aw of the cornmeal powders was described using several sorption models (Chapter 2, section 2.1.6) as shown in Table 4.13. The model which best fitted the isotherm was determined by the R-squared value. Based on the R^2 value, Peleg model (equation 2.12) yielded a fit with a value of 0.999. However, this model consists of four parameters which is the highest as compared to other models. This model is a purely empirical model without a theoretical background and gave a Sum of Squared Errors (SSE) of prediction values ranging from 0.524 to 0.756 for different concentrations of calcium stearate. Peleg (1993), Rahman *et al.* (1997) and Delgado and Sun (2002) reported that this model has been good in determining the isotherms for potato starch, peas and cured beef. One disadvantage is that this model is not based on the assumption that there exists a well-defined monolayer of absorbed water unlike the GAB and BET models (equation 2.9 and 2.4) (Peleg, 1993).

GAB is the best model as it fitted the data with an R^2 value of 0.99 and used lesser parameters to determine the moisture isotherms. The monolayer moisture content for GAB model was highest at 0.5% wt/wt concentration of calcium stearate indicating that the samples will remain stable with a higher amount of moisture present in it. Other models evaluated in this study were also able to predict the isotherm for cornmeal powder with an R^2 value of 0.99 but were then further analyzed based on the SSE value. Ferro-Fontan model (eq. 2.8) having SSE value ranging from 1.792 to 2.895, GAB having values for SSE ranging from 3.009 to 5.585, and Oswin (eq. 2.7) model having values for SSE ranging from 1.210 to 5.898. Henderson model (eq. 2.6) was also able to predict the values with the same R^2 value but had error greater than Oswin, Ferro-Fontan, GAB, and Peleg model, however, it was more accurate when compared with Modified-BET (eq. 2.3), Hasley (eq. 2.4), and Smith (eq. 2.5). Figures 4.12 to 4.16 show the predicted plots for Henderson, Oswin, Ferro-Fontan, GAB, and Peleg model, respectively. The disadvantage of Peleg model is that it doesn't incorporate the monolayer adsorption in the equation. Due to this reason, GAB model is usually preferred as it is a theoretical model and has been derived from Langmuir and BET models. GAB model assumes that the molecular layers at the saturation pressure in a small number.

Halsey model least adequately represented the experimental data with and R^2 value of 0.78. Henderson, GAB, Ferro-Fontan, Peleg, and Oswin models were able to predict the isotherms for all the samples while Modified BET, Smith, and Halsey models were inadequate in predicting the isotherms.

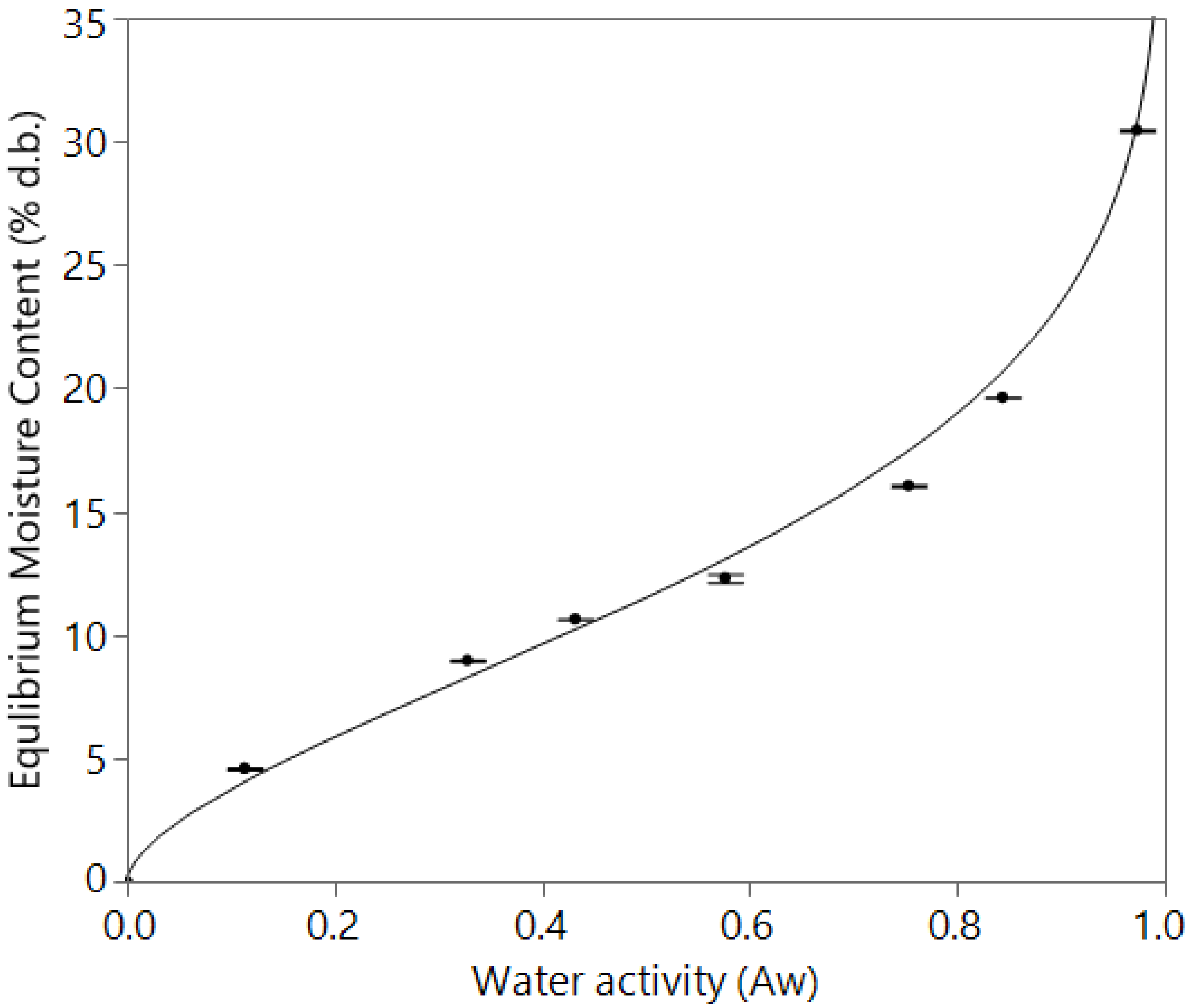


Figure 4.12. Sorption isotherm for cornmeal powder at 0.50% concentration of calcium stearate (wt/wt) at 25°C predicted using Henderson model, R^2 = 0.993 (solid line, Equation 2.6).

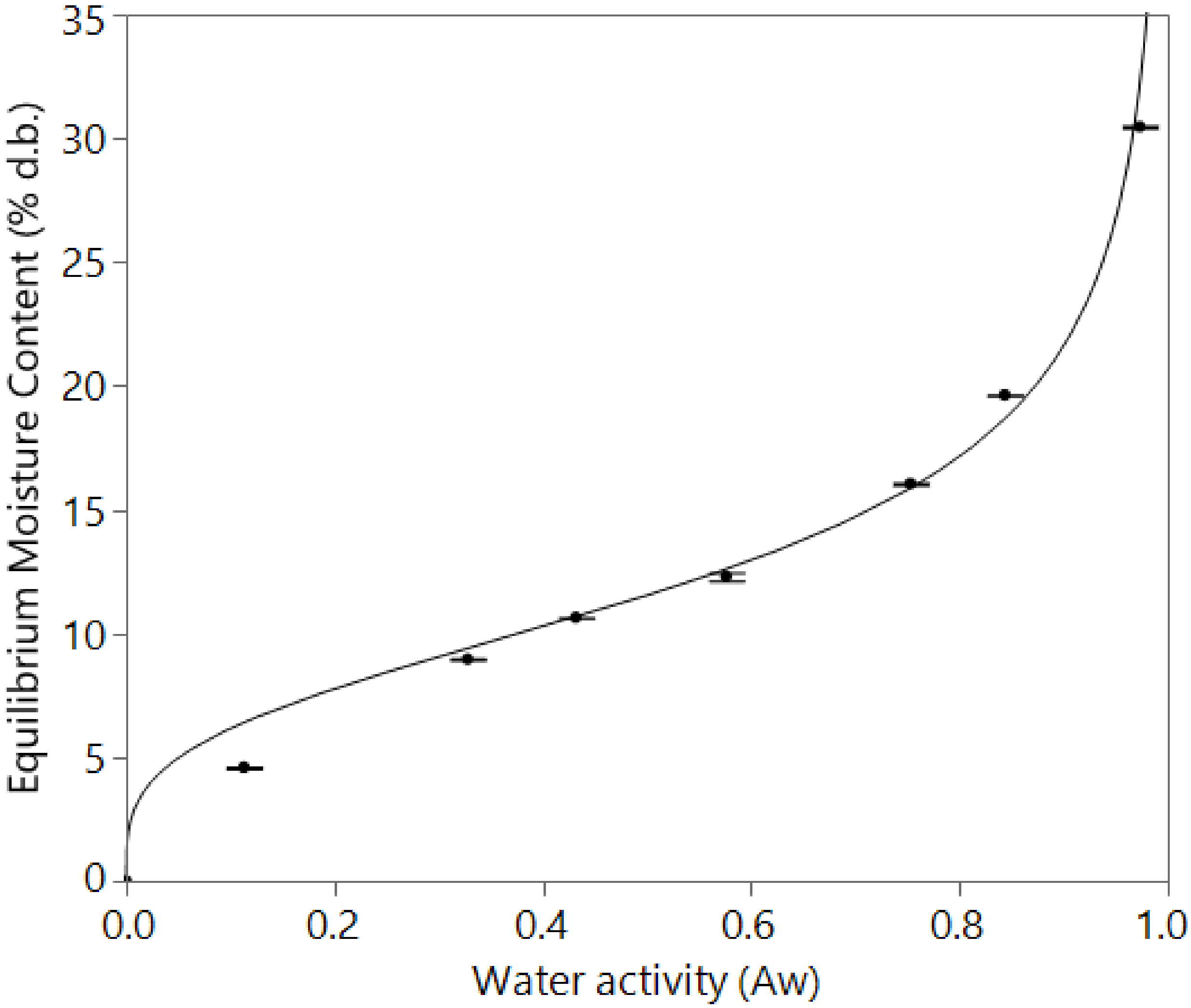


Figure 4.13. Figure 4.12. Sorption isotherm for cornmeal powder at 0.50% concentration of calcium stearate (wt/wt) at 25°C predicted using Oswin model, R^2 = 0.988 (solid line, Equation 2.7).

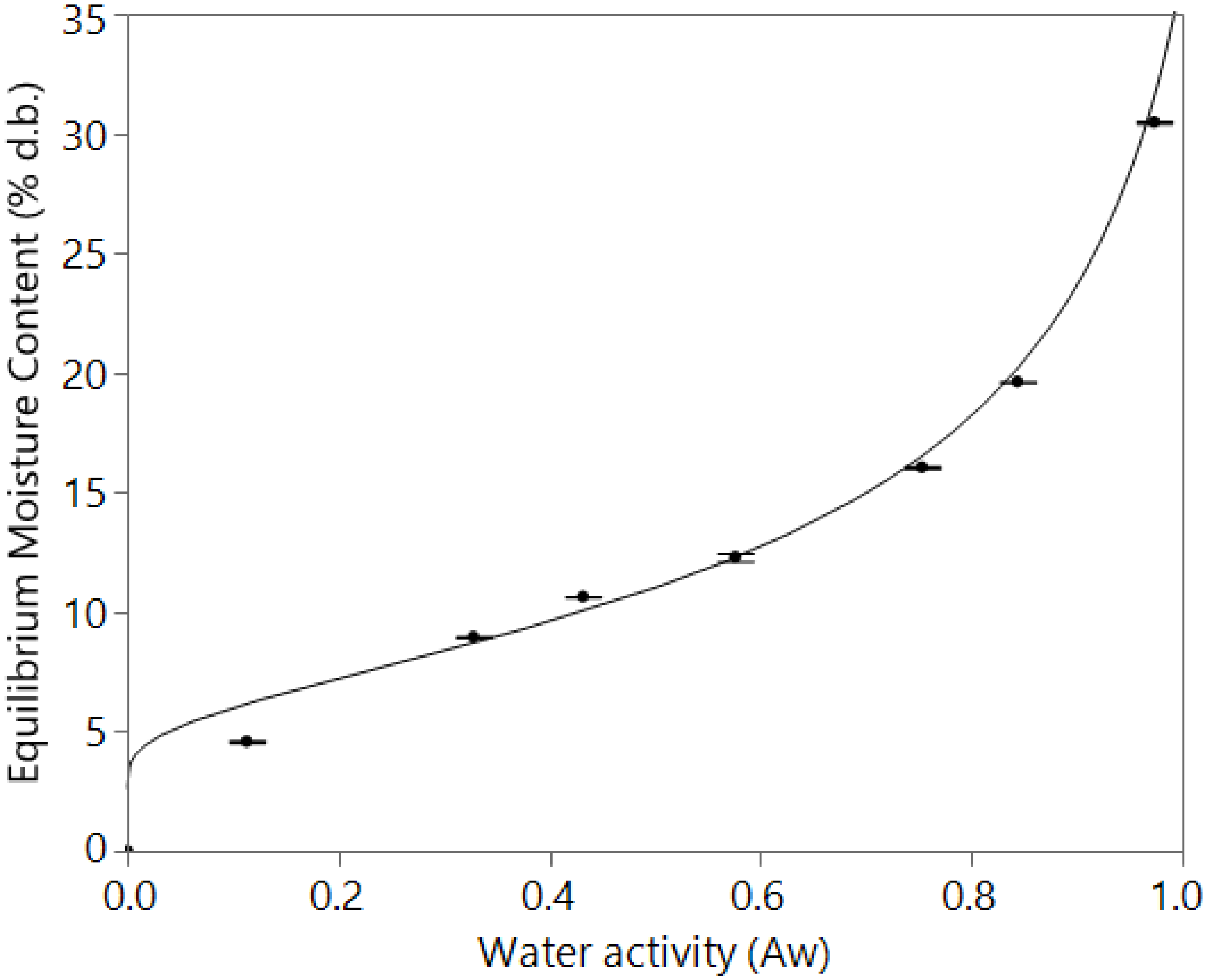


Figure 4.14. Sorption isotherm for cornmeal powder at 0.50% concentration of calcium stearate (wt/wt) at 25°C predicted using Ferro-Fontan model, R^2 = 0.992 (solid line, Equation 2.8).

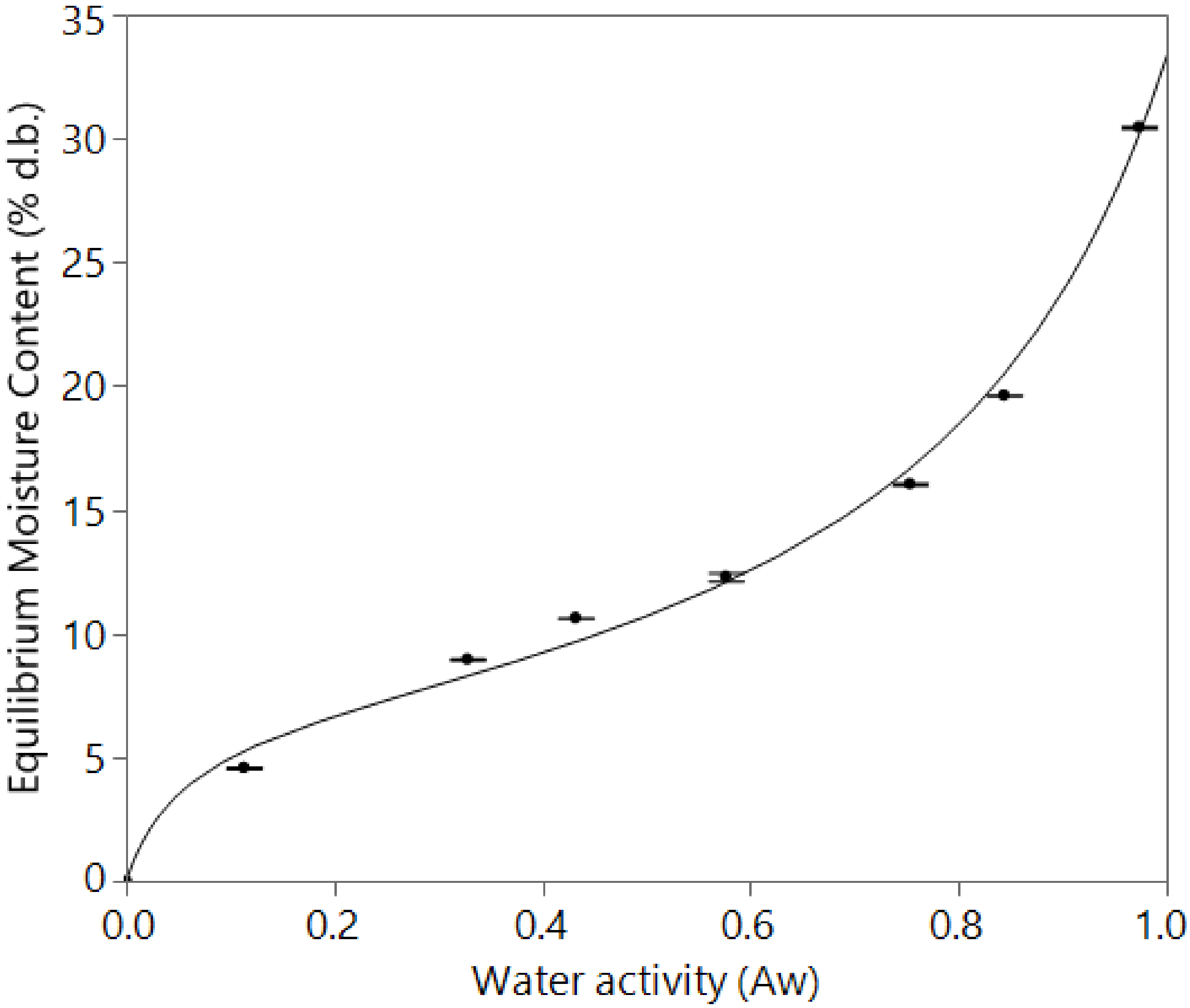


Figure 4.15. Sorption isotherm for cornmeal powder at 0.50% concentration of calcium stearate (wt/wt) at 25°C predicted using GAB model, $R^2 = 0.994$ (solid line, Equation 2.9).

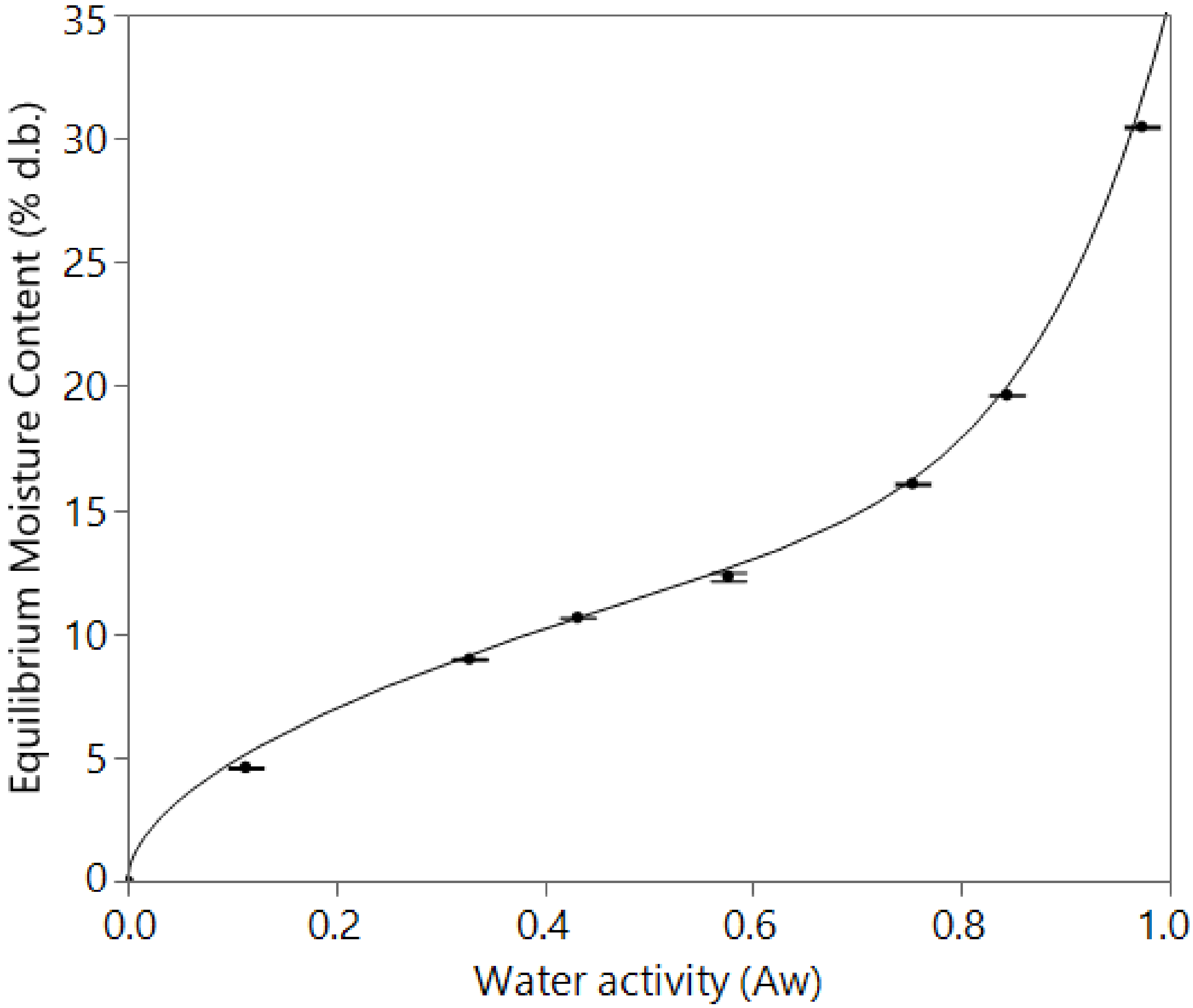


Figure 4.16. Sorption isotherm for cornmeal powder at 0.50% concentration of calcium stearate (wt/wt) at 25°C predicted using Peleg model, $R^2 = 0.999$ (solid line, Equation 2.12).

Table 4.13. Parameters for the sorption models evaluated in this study for cornmeal powder at 25°C

Model	**Parameters**	**Calcium Stearate (wt/wt)**			
		0%	**0.50%**	**0.75%**	**1.00%**
Modified-BET (eq. 2.3)	X_0	3.835	3.725	3.948	3.956
	C	1.01×10^8	1.23×10^8	1.38×10^8	1.01×10^8
	SSE	276.601	278.37	281.866	283.254
	MSE	46.102	46.396	46.977	47.209
	RMSE	6.789	6.811	6.854	6.870
Halsey (eq. 2.4)	A	1234.969	1278.092	1390.199	1394.030
	B	3.080	3.117	3.090	3.089
	SSE	13.231	51.87	8.710	9.113
	MSE	2.672	2.730	1.742	1.822
	RMSE	1.634	1.652	1.319	1.350
Smith (eq. 2.5)	A	4.449	4.387	4.698	4.702
	B	-7.907	-7.680	-8.046	-8.066
	SSE	30.071	32.223	31.880	32.272

Table 4.13. Continued

Model	**Parameters**	**Calcium Stearate (wt/wt)**			
		0%	**0.50%**	**0.75%**	**1.00%**
	MSE	5.011	5.370	5.313	5.378
	RMSE	2.238	2.317	2.305	2.319
Henderson (eq. 2.6)	A	1.681	1.705	1.700	1.699
	B	0.011	0.011	0.010	0.103
	SSE	5.039	3.354	9.458	9.575
	MSE	0.839	0.559	1.576	1.595
	RMSE	0.916	0.747	1.255	1.263
Oswin (eq. 2.7)	A	11.541	11.339	11.892	11.914
	B	0.285	0.282	0.284	0.284
	SSE	3.545	5.898	1.210	1.463
	MSE	0.590	0.983	0.201	0.243
	RMSE	0.768	0.991	0.449	0.493
Ferro Fontan (eq. 2.8)	γ	65.083	48.057	129.46	128.705

Table 4.13. Continued

Model	**Parameters**	**Calcium Stearate (wt/wt)**			
		0%	**0.50%**	**0.75%**	**1.00%**
	α	1.088	1.113	1.055	1.055
	r	1.845	1.721	2.115	2.111
	SSE	1.792	2.895	1.818	2.156
	MSE	0.448	0.723	0.454	0.539
	RMSE	0.669	0.850	0.674	0.734
GAB (eq. 2.9)	X_0	6.711	6.860	6.670	6.696
	C	34.154	23.122	66.787	63.452
	K	0.808	0.796	0.814	0.814
	SSE	3.009	3.136	5.234	5.585
	MSE	0.601	0.627	1.046	1.117
	RMSE	0.775	0.791	1.023	1.056
Peleg (eq. 2.12)	K_1	177.033	123.405	259.649	245.336
	K_2	1.431	1.404	1.383	1.377

Table 4.13. Continued

Model	Parameters	Calcium Stearate (wt/wt)			
		0%	**0.50%**	**0.75%**	**1.00%**
	n_1	0.544	0.589	0.511	0.518
	n_2	8.183	8.372	9.253	9.390
	SSE	0.524	0.121	0.433	0.756
	MSE	0.131	0.030	0.108	0.189
	RMSE	0.362	0.174	0.329	0.434

X_0, A, B, K, K_1, K_2, n_1, n_2 are parameters for the models (Chapter 2, Table 2.2)

SSE: Sum of squared errors of prediction

MSE: Mean squared error

RMSE: Root mean-square error

4.1.9. Hygroscopicity

Hygroscopicity of cornmeal powder was classified based on the moisture isotherms specified in section 2.1.6. The samples gained approximately 9% MC (w.b.) when stored at 43% RH at 25°C. This falls in Class IV of hygroscopicity classification (Chapter 3, Table 3.3), which states that there is an increase in moisture content (d.b.) when the sample is exposed to a RH between 40-50% and at RH greater than 90% for one week; the MC increase is greater than 30% (d.b.). This classification helps us understand that moisture content will greatly vary depending on the RH of the environment since cornmeal powder belongs to Class IV. Thus, the cornmeal powder evaluated in this study is classified as a very hygroscopic powder that needs proper storage conditions i.e. low relative humidity environment, to prevent increase in moisture content.

The degree of hygroscopicity was also quantified using the slope of the linear part of the sorption isotherm (g H_2O/100 g dry sample/a_w) in region II generated for the various samples for cornmeal powder (Figure 4.17). The slopes of moisture isotherms for the different samples were found which gave the values of slope in g H_2O/100 g dry sample/a_w. The slopes of the moisture isotherms in region II were significantly different ($p<0.05$) for the all the samples except for samples at 17.0% and 20.0% (w.b.) moisture content from table 4.14. The amount of moisture uptake was the lowest for the samples with 1.00% wt/wt concentration of calcium stearate which was not significantly different ($p<0.05$) from the samples with 0.75% wt/wt concentration of calcium stearate. The samples without conditioner had the highest value of the water uptake in the region II signifying that these samples were more hygroscopic as compared to samples with conditioner.

Based on the degree of hygroscopicity of the samples, all the sample can be considered to be good adsorbers of moisture. This can be corroborated by the fact that the samples were classified as Class IV hygroscopic materials. A flatter curve in the region II having relatively no slope would have indicated a sample that is bad adsorber of moisture. Due to the hygroscopic nature of the cornmeal samples, it was found that the samples gained approximately 16 g H_2O per 100 g dry sample/a_w for all the samples which signifies a large increase.

Increasing the concentration of calcium stearate decreased the moisture adsorbed by the samples. This means that the sample becomes less hygroscopic with increasing concentration of calcium stearate. The sample therefore would be best stored at 1.00% and 0.75% wt/wt calcium stearate concentration as they have the lowest slope for all regions of the moisture isotherm.

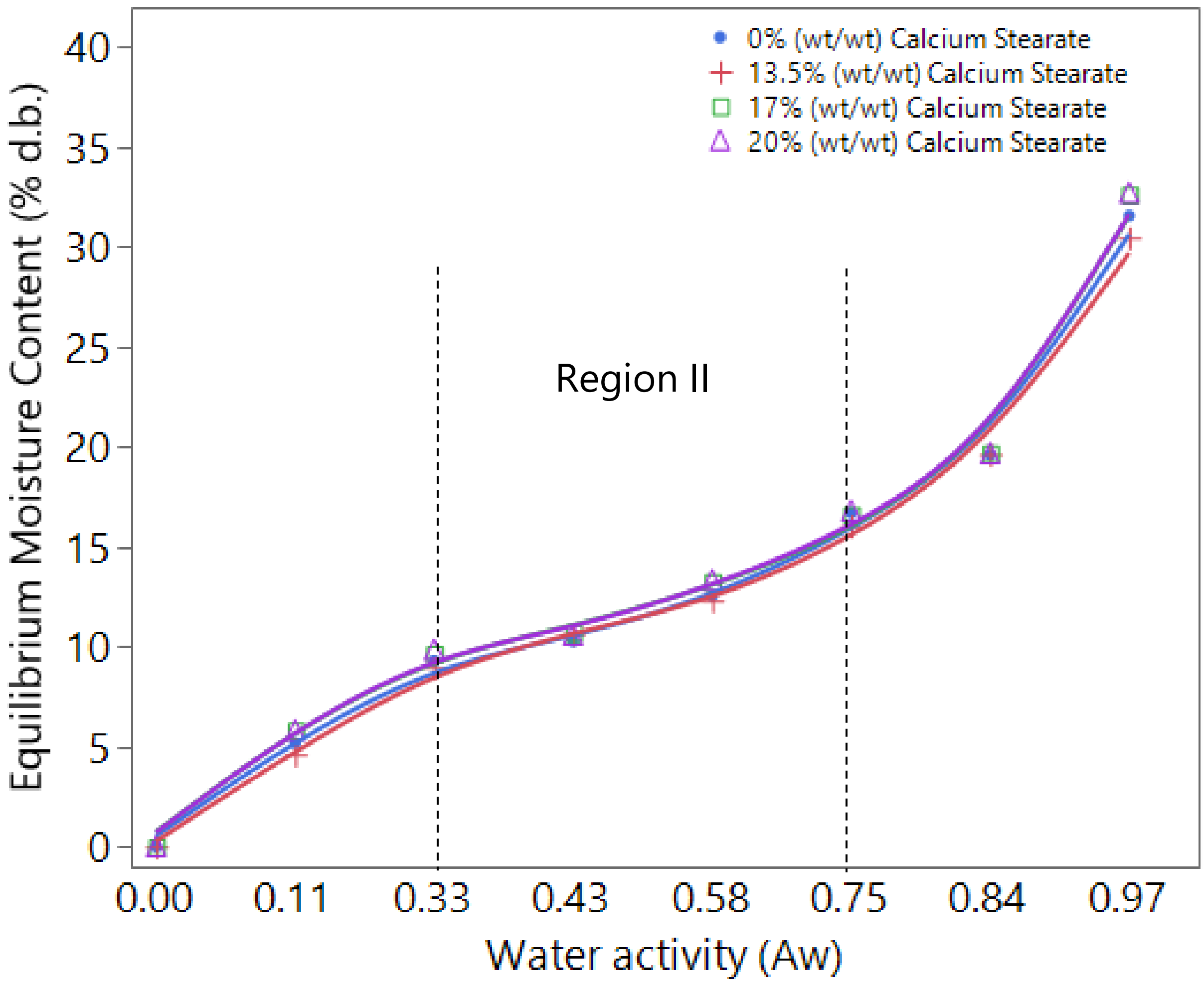
Table 4.14. Degree of hygroscopicity based on the slope of moisture isotherms of cornmeal powder (% EMC (d.b.)/a_w) with varying concentrations of calcium stearate at 25°C.

Region	**Calcium Stearate (wt/wt)**			
	0.00%	**0.50%**	**0.75%**	**1.00%**
Region II	$_x$17.45 ± 0.08	$_y$16.67 ± 0.12	$_z$16.38 ± 0.08	$_z$16.36 ± 0.17

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(x-w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($p < 0.05$).

Figure 4.17. Region II of moisture isotherm of cornmeal powder for quantification of the degree of hygroscopicity at 25°C



4.2. Flow properties of cornmeal powder

4.2.1. Flow function

Figures 4.18 through 4.22 show the flow behavior of the powders at different moisture contents and calcium stearate concentrations in terms of their flow functions. A linear increase in Unconfined Failure Strength (UFS in kPa) was found as the Major Principal Consolidation Stress (MPCS in kPa) increased.

The inverse of the slope of the lines represents the flow index, which increased in counter clockwise direction (figures 4.18 to 4.22), and it indicates increasing flowability. This is due to the fact that the powder will start flowing on application of a small amount of stress (UFS). A flow index value greater than 10 indicates excellent flow. However, none of the sample tested fell in that region. The best flow behavior was for cornmeal sample at 0.50% calcium stearate concentration and 10.0% moisture content (w.b.) with a value of 6.70 indicating good flow. The addition of calcium stearate increased the flow index at 0.50% concentration but then observed a decreasing trend. This might be due to the fact that calcium stearate acts as a conditioner only to an extent, beyond which its impact is negative. At 0% wt/wt concentration of calcium stearate, the highest value for flow index was 6.47 at 10.0% MC (w.b.) and it decreased with increasing MC.

According to Jenike's classification (Fitzpatrick *et al.*, 2004), a flow index value greater than 4 represents easy flowing materials. At 0% wt/wt concentration of calcium stearate, cornmeal powder at 10.0%, 13.5% and 17.0% moisture content (w.b.) have flow index values as 6.47 ± 0.192, 4.70 ± 0.050 and 4.58 ± 0.162 respectively. As these values are greater than 4, according to Jenike's classification the cornmeal powder at 0% wt/wt concentration of calcium stearate with 10.0%, 13.5% and 17.0% moisture content would be considered as easy flowing. However, at 0% wt/wt concentration of calcium stearate and 20.0% MC, the flow index is 3.82 ± 0.048 which is lesser than 4 and Jenike's classification would classify the cornmeal powder as cohesive. With the increase in MC, the samples started gaining strength because of the cohesion between the particles. As the moisture content increases from 10.0% to 20.0% the flow index value reduces from 6.47 ± 0.192 to 3.82 ± 0.048. According to Jenike's classification, decreasing flow index with increasing moisture content represents cohesiveness between the particles. Statistically, the means are significantly different ($p<0.05$) at increasing moisture content.

There is a direct correlation between the size of particles and the flowability of the powders, though moisture content played a more influential role in decreasing the flowability as the particle size increased with increasing MC. At 0% wt/wt calcium stearate, the particle size increased with increasing moisture content with the highest value being 610.2 µm at 20.0% moisture content (w.b.). The expected trend was an increase in the flow index as the size of particle is directly related to the flowability. However, the value of flow index at 20.0% moisture content (w.b.) and 0% concentration of calcium stearate is 3.82 ± 0.05 which is lower than all the values at different mositure contents at 0% calcium stearate. This trend is explained by the increase in cohesive forces due to increase in moisture content.

At fixed moisture levels, the flow index was the lowest (value) for cornmeal powder with 0.50% wt/wt calcium stearate. The flow index at 10.0% MC (w.b.) had the highest value of 6.70 for 0.50% wt/wt calcium stearate and decreased from 6.47 to 5.79 for increasing concentration of calcium stearate (Table 4.15 and Figure 4.19). Hence, the introduction of calcium stearate enhanced the flow behavior of the cornmeal powder and had a significant effect ($p<0.05$) at 0.50% wt/wt. This result is probably due to the fact that the calcium stearate particles fill up the voids and act as a lubricant (reference). The effect was not very pronounced at higher concentrations of calcium stearate as other factors such as van der waal force, mechanical interactions, and small particle size of calcium stearate overpowered its lubricant effect. Oginni (2014) also noticed that the flowability of ground loblolly pine samples decreased on addition of smaller particles as they filled up the vacant spaces and caused a reduction in the voids.

In general, the flowability of powders decreases with decreasing particle size due to the increase in the surface area per unit mass, which increases the friction between the particles. In addition, the flowability of the powders decrease with an increase in moisture content. However, both these effects can sometimes act in tandem or in opposition to each other. Fitzpatrick *et al.* (2004) found that a decrease in particle size of salt increased the cohesiveness of the milk powder. There are exceptions to this trend and Fitzpatrick *et al.* (2004) noticed that tomato powder with largest particle size amongst all samples tested had a lower flow index which was explained due to the high moisture content that led to increased cohesiveness which is defined as building of liquid bridges with the increase of moisture. Fitzpatrick *et al.* (2004) discusses the various components that affect cohesion in the milk powder such as effect of particle size, free-fat content, temperature and moisture content.

The particle size of cornmeal powder increased with the increase in the moisture content but the flowability decreased. A similar trend was observed by Fitzpatrick *et al.* (2004) in case of tomato powder for which the increase in moisture was responsible for creating liquid bridges and increasing the cohesion between the particles, which impeded the flow of tomato powder at high moisture contents. According to Jenike's classification, the flow index of 6.47 at 10.0% MC (w.b.) (0% conditioner) represents good flow with very little or no cohesive behavior whereas samples at 20.0% moisture content (w.b.) and calcium stearate concentration 0%, 0.75%, and 1.00% represent bad flow behavior and fall in the cohesive region of Jenike's classification. Even though particle size and moisture content significantly affect the flowability, there are other factors too that are responsible for change in flow behavior such as wall friction, internal friction, surface characteristics. etc.

The relationship of the flow index with moisture content (both in wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$ff_c = 8.64 - 0.23 \times MC(w.b.) - 0.13 \times CS\left(\%\frac{wt}{wt}\right) \quad (4.9a)$$

$$ff_c = 8.13 - 0.16 \times MC(d.b.) - 0.13 \times CS\left(\%\frac{wt}{wt}\right) \quad (4.9b)$$

where ff_c is flow index, MC is the moisture content, and CS is calcium stearate

Table 4.15. Flow index of cornmeal powder at varying moisture content and calcium stearate concentration at 25°C

MC (w.b.)	Calcium Stearate (wt/wt)			
	0.00%	**0.50%**	**0.75%**	**1.00%**
10.0%	$_{x,y}6.47^{a} \pm 0.19$	$_{x}6.70^{a} \pm 0.28$	$_{y}6.14^{a} \pm 0.06$	$_{z}5.79^{a} \pm 0.13$
13.5%	$_{x}4.70^{b} \pm 0.05$	$_{y}5.85^{b} \pm 0.30$	$_{y}5.59^{b} \pm 0.24$	$_{z}5.15^{b} \pm 0.12$
17.0%	$_{x}4.58^{b} \pm 0.16$	$_{y}5.00^{c} \pm 0.18$	$_{x}4.67^{c} \pm 0.07$	$_{z}4.23^{c} \pm 0.08$
20.0%	$_{x}3.82^{c} \pm 0.05$	$_{y}4.15^{d} \pm 0.28$	$_{x,y}3.91^{d} \pm 0.14$	$_{x}3.72^{d} \pm 0.04$

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a-d)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($P < 0.05$).

$^{(x-w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($P < 0.05$).

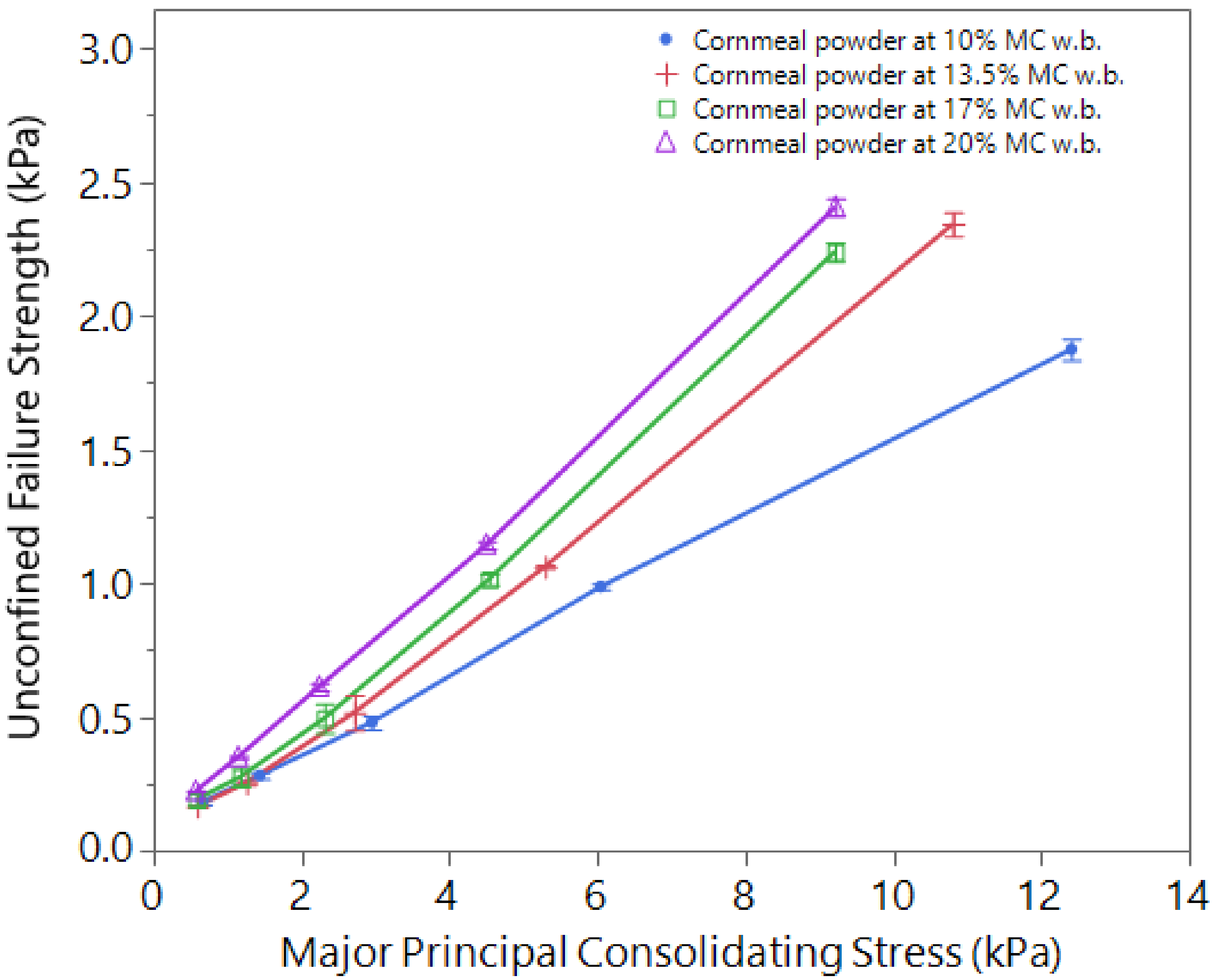


Figure 4.18. Flow function of cornmeal powder without conditioner at 25°C

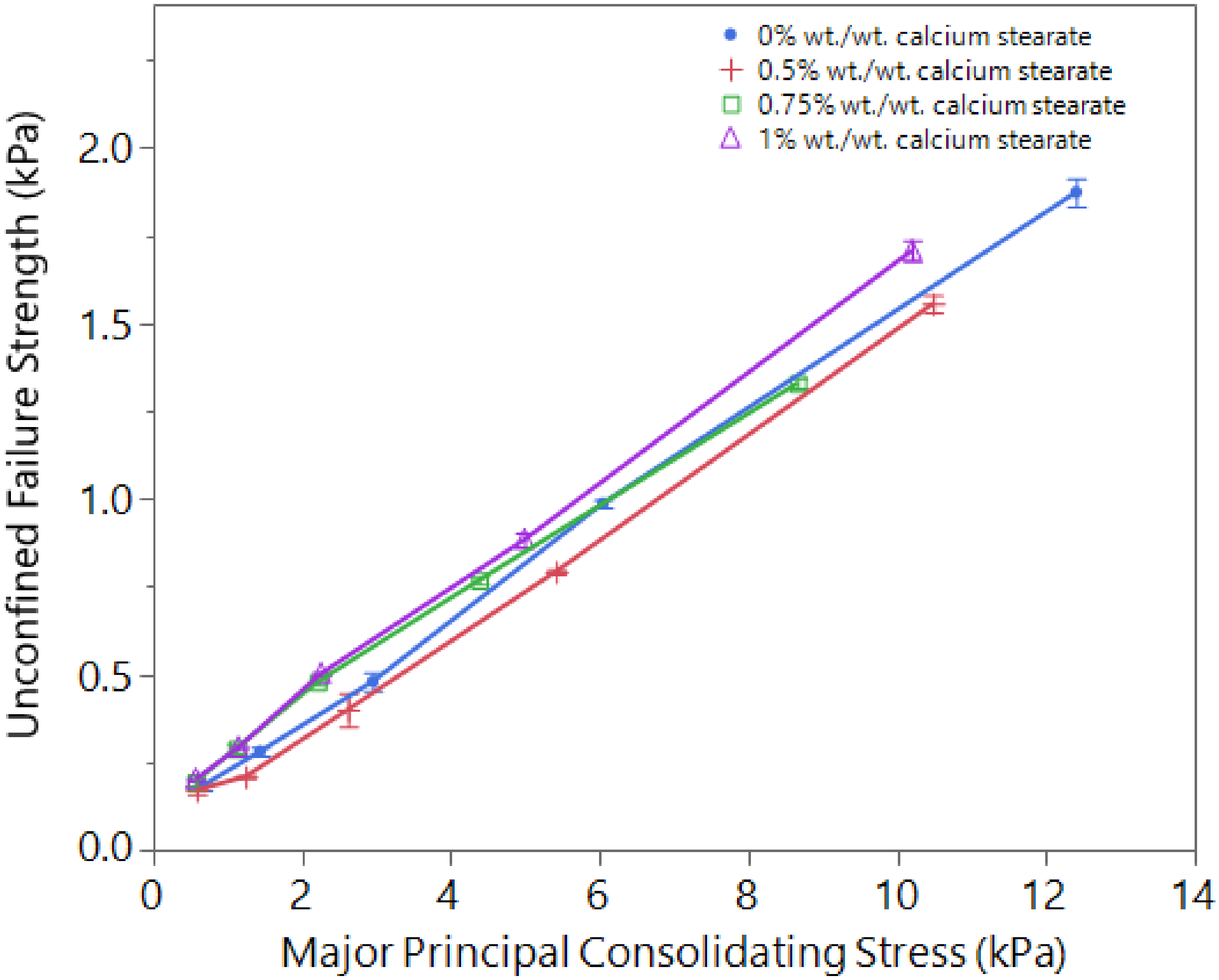


Figure 4.19. Flow function of cornmeal powder at 10.0% MC at 25°C

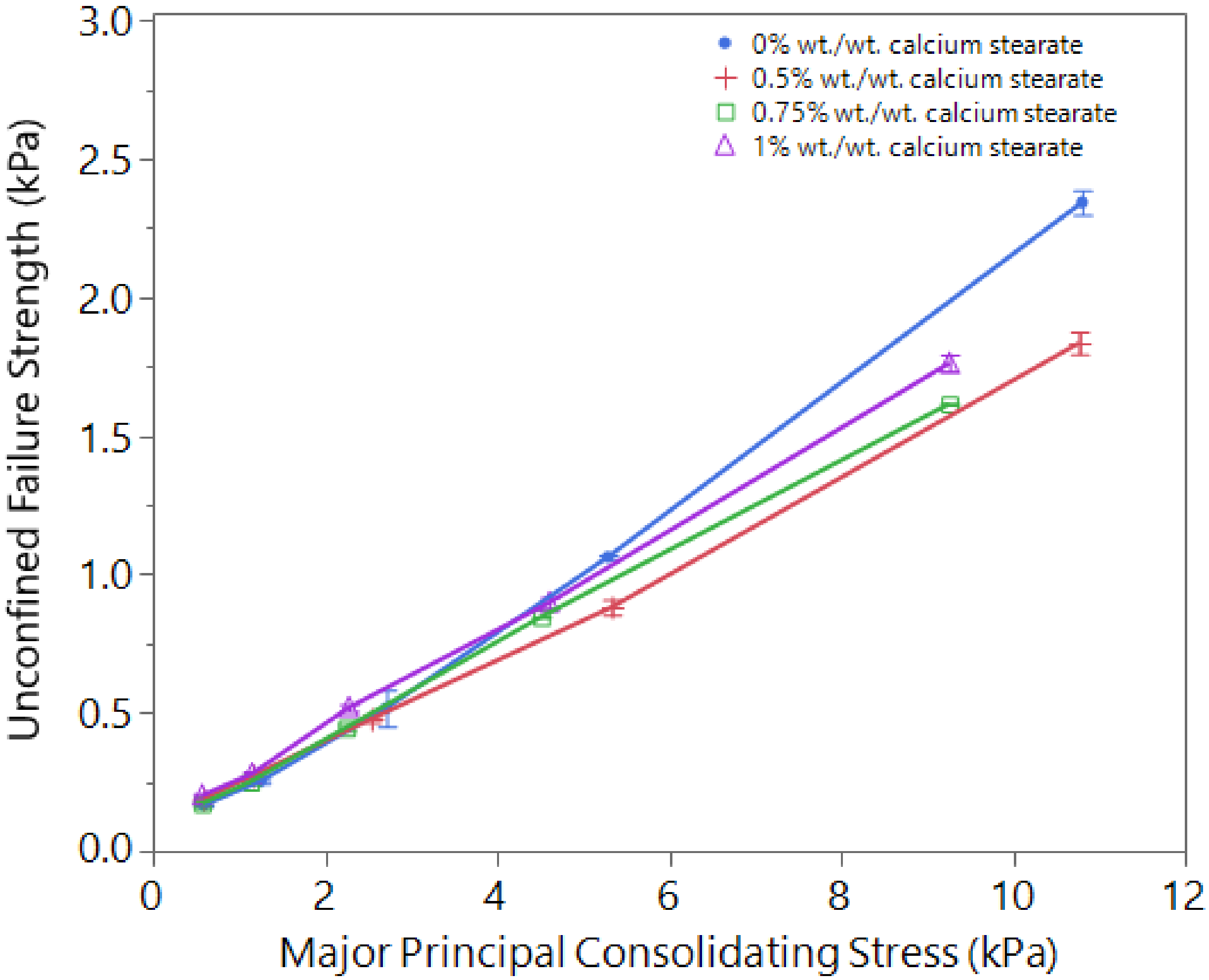


Figure 4.20. Flow function of cornmeal powder at 13.5% MC at 25°C

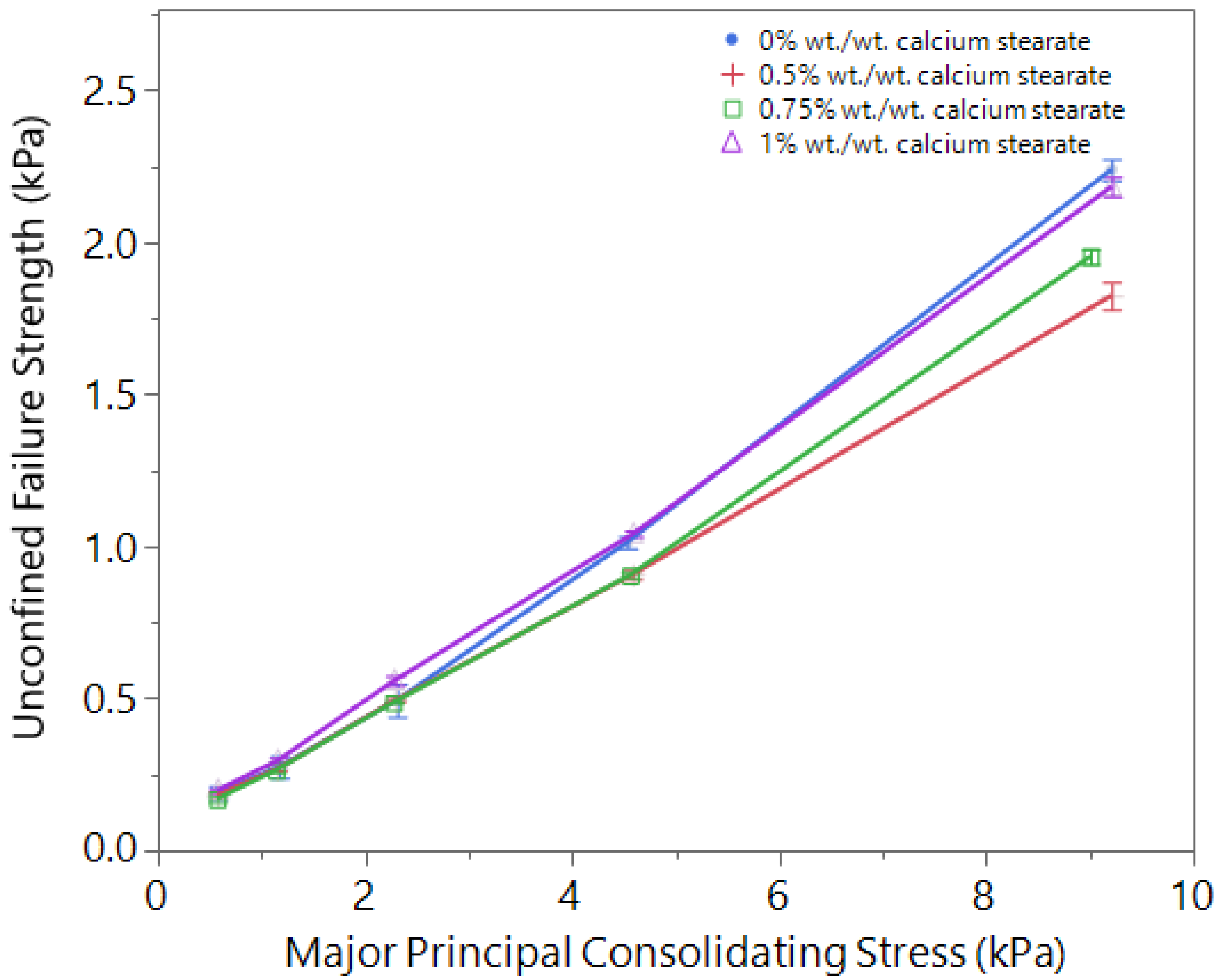


Figure 4.21. Flow function of cornmeal powder at 17.0% MC at 25°C

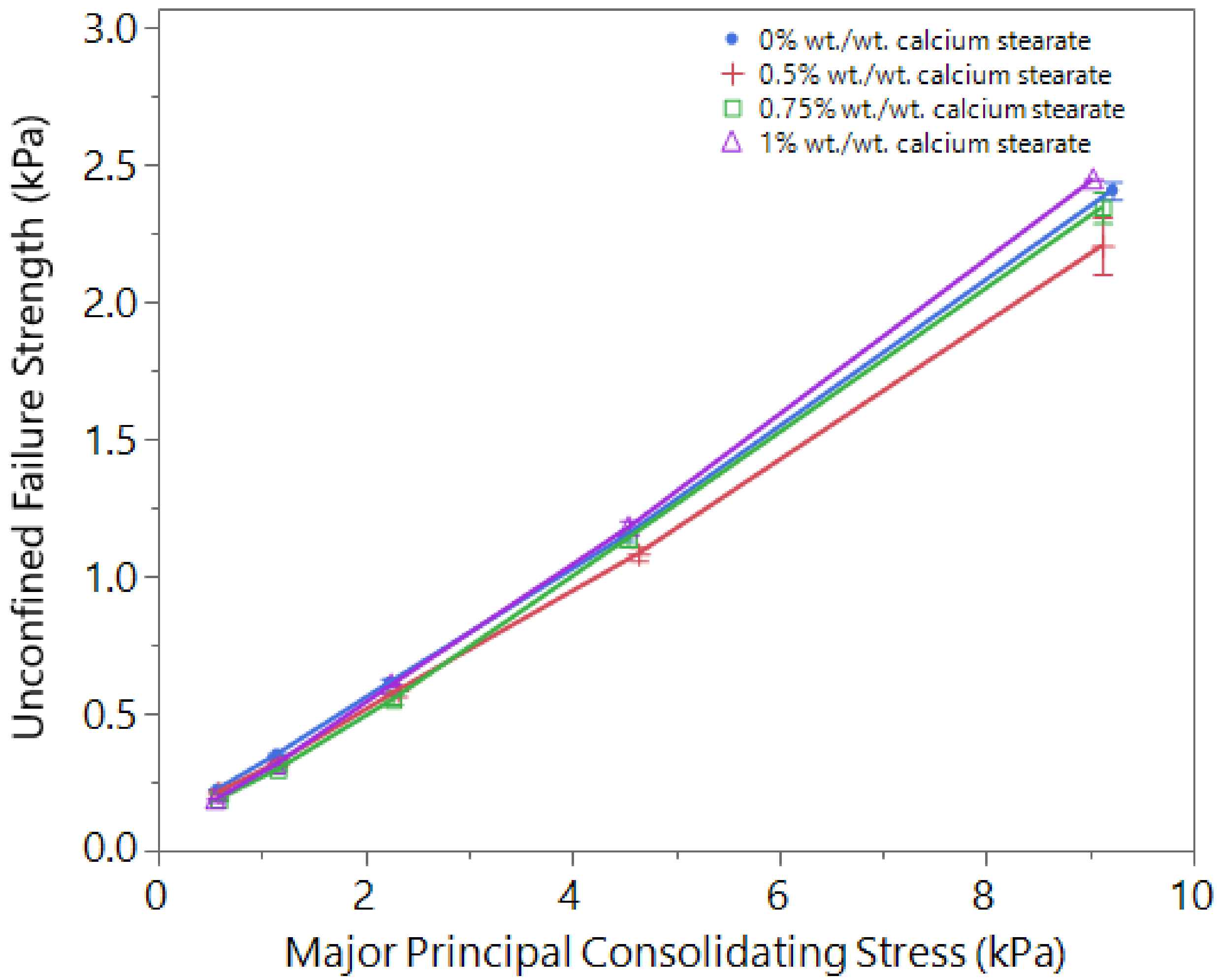


Figure 4.22. Flow function of cornmeal powder at 20.0% MC at 25°C

4.2.2. Angle of internal friction

Table 4.16 shows the values for angle of internal friction obtained for cornmeal powder at varying moisture levels and concentrations of calcium stearate. A decrease in the angle of internal friction leads to less resistance between particles of the sample and therefore it represents better flow behavior. However, the angle of internal friction alone cannot be considered to be the most dominant factor. It was noted by Mohsenin (1970) and Peleg *et al.* (1973) that the moist powders exhibit cohesion despite suffering a decrease in the angle of internal friction.

The angle of internal friction was significantly ($p<0.05$) different at fixed moisture levels with varying concentration of calcium stearate. Peleg *et al.* (1973) noted a decrease in the angle of internal friction for powdered sucrose on addition of calciums stearate. The angle decreased to a minimum value at 0.75% wt/wt calcium stearate for moisture levels 10.0%, 13.5%, and 17.0% (w.b.). This result suggests that the calcium stearate particles act as lubricant thus decreasing the friction between the particles of cornmeal powder. This finding is supported by our previous result (section 4.9).

The internal friction angle varied significantly ($p<0.05$) from 40.37° to 37.68° at 0% wt/wt calcium stearate. This decrease is contrary to the expected result and can be explained based on the increase in particle size. The increase in the particle size with increasing MC reduces the friction between the particles as they spread out in the bulk and have less contact area. A similar trend was seen for samples at 0.50% wt/wt concentrations of calcium stearate for MC vaying between 10.0% and 17.0% (w.b.). For concentrations 0.75% and 1.00% of calcium stearate, the trend was not statistically significant ($p>0.05$). The best combination of moisture content and calcium stearate concentration is 10.0% mositure content (w.b.) and 0.75% wt/wt, respectively. The worse condition for flowability will be at 13.5% moisture content (w.b.) and 0% wt/wt calcium stearate.

The relationship of the flow index with moisture content (both in wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$\varphi_i\text{=39.87-0.01×MC(w.b.)-1.46×CS}\left(\%\frac{\text{wt}}{\text{wt}}\right) \tag{4.10a}$$

$$\varphi_i\text{=39.86-0.01×MC(d.b.)-1.46×CS}\left(\%\frac{\text{wt}}{\text{wt}}\right) \tag{4.10b}$$

where φ_i is angle of internal friction MC is the moisture content, and CS is calcium stearate

Table 4.16. Angle of internal friction (°) of cornmeal powder at varying moisture content and calcium stearate concentration at 25°C

MC (w.b.)	**Calcium Stearate (wt/wt)**			
	0.00%	**0.50%**	**0.75%**	**1.00%**
10.0%	$_x40.37^a \pm 0.34$	$_y39.32^{a,b} \pm 0.17$	$_z36.86^a \pm 0.44$	$_w38.65^a \pm 0.07$
13.5%	$_x41.26^b \pm 0.20$	$_y39.12^{b,c} \pm 0.06$	$_y37.42^{a,b} \pm 0.46$	$_z38.70^a \pm 0.25$
17.0%	$_x39.66^c \pm 0.24$	$_y38.56^c \pm 0.43$	$_y37.96^{b,c} \pm 0.28$	$_z39.06^b \pm 0.25$
20.0%	$_x37.68^d \pm 0.24$	$_y39.82^a \pm 0.42$	$_z38.29^c \pm 0.39$	$_z38.97^{a,b} \pm 0.02$

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a\text{-}d)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($P < 0.05$).

$^{(x\text{-}w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($P < 0.05$).

4.2.3. Angle of wall friction

The angle of wall friction was statistically different (p<0.05) for increasing moisture content at fixed concentrations of calcium stearate (Table 4.17). At a fixed moisture content, the angle of wall friction generally decreased.

At higher moisture contents, the particles of the sample adhered to the wall of the instrument strongly, giving a higher value for wall friction angle. The angle of wall friction had the lowest value of 11.21 ± 0.18° for the sample with 1.00% wt/wt calcium stearate at 10.0% MC (w.b.).

The increase in the wall friction angle due to increase in the MC has been reported by Davies *et al.* (2009) and Fitzpatrick *et al.* (2004) for biological powder materials. Fitzpatrick *et al.* (2004) reported a similar trend for tea and whey permeate with increasing MC.

The relationship of the flow index with moisture content (both in wet and dry basis) and concentration of calcium stearate at 25°C is given by:

$$\varphi_w = 10.17 + 0.31 \times \text{MC(w.b.)} - 2.44 \times \text{CS}\left(\%\frac{\text{wt}}{\text{wt}}\right) \quad (4.11a)$$

$$\varphi_w = 10.84 + 0.22 \times \text{MC(d.b.)} - 2.44 \times \text{CS}\left(\%\frac{\text{wt}}{\text{wt}}\right) \quad (4.11b)$$

where φ_i is angle of wall friction (°), MC is the moisture content, and CS is calcium stearate

Table 4.17. Angle of wall friction (°) of cornmeal powder at varying moisture content and calcium stearate concentration at 25°C

MC (w.b.)	Calcium Stearate (wt/wt)			
	0.00%	**0.50%**	**0.75%**	**1.00%**
10.0%	$_{x}12.88^{a} \pm 0.08$	$_{y}11.88^{a} \pm 0.48$	$_{z}11.30^{a} \pm 0.13$	$_{z}11.21^{a} \pm 0.18$
13.5%	$_{x}15.41^{b} \pm 0.10$	$_{y,z}12.80^{b} \pm 0.40$	$_{z}12.26^{b} \pm 0.15$	$_{y}12.93^{b} \pm 0.46$
17.0%	$_{x}15.06^{c} \pm 0.15$	$_{y}13.50^{b} \pm 0.33$	$_{y}13.33^{c} \pm 0.28$	$_{y}13.75c \pm 0.30$
20.0%	$_{x}17.71^{d} \pm 0.15$	$_{y}15.01^{c} \pm 0.43$	$_{z}13.58^{c} \pm 0.13$	$_{w}14.36^{d} \pm 0.12$

The data is represented as: Mean ± SD. Values are means of 3 replications.

$^{(a\text{-}d)}$ Means within a column, which are not followed by a common superscript letter, are significantly different ($P < 0.05$).

$^{(x\text{-}w)}$ Means within a row, which are not followed by a common subscript letter, are significantly different ($P < 0.05$).

4.3. Correlation between physical properties and flow behavior of cornmeal samples

4.3.1. Relationship of Hausner's Ratio (HR) and Carr's Index (CI) with porosity, particle size, and angle of repose

The HR and CI did not correlate well with the porosity of the cornmeal samples and did not exhibit a definite pattern (Figures 4.23 and 4.24). From table 4.18, the correlation was found to be 0.25 which means that it is a weak linear relationship. The values for HR and CI are therefore not predictable based on the porosity of the samples.

The correlation of HR and CI with particle size was 0.36 (Table 4.18) which signifies a weak positive linear relationship (Figures 4.25 and 4.26). The prediction expression for HR and

CI with particle size had an R-squared value of 0.13 and therefore were not used to estimate the properties.

An increase in HR and CI represent reduced flowability whereas an increase in the particle size indicates an increase in flowability of the powder. Since the correlation between the terms was positive, the effect of HR and CI overpowered the effect of particle size on flowability which overall decreased with increasing moisture content.

Hausner's Ratio and Carr's Index increased with increasing angle of repose indicating decreased powder flowability. The linear relationships of HR and CI with the angle of repose were best described (Figure 4.27 and 4.28) using the following equations:

$$HR=-0.25+0.03\times\alpha \tag{4.12}$$

where HR is the Hausner's Ratio, and α is the angle of repose (degree)

$$CI=-85.81+2.59\times\alpha \tag{4.13}$$

where CI is the Carr's Index, and α is the angle of repose (degree)

HR and CI can be predicted based on the above equations with an R-squared value of 0.79. The correlation was found to be 0.88 which signifies a strong positive linear relationship.

Table 4.18. Relationship of Hausner's Ratio and Carr's Index with porosity, particle size, and angle of repose.

		Porosity	Particle size	Angle of repose
Hausner's Ratio/Carr's Index	R^2	0.06	0.13	0.79
	Correlation	0.25	0.36	0.88

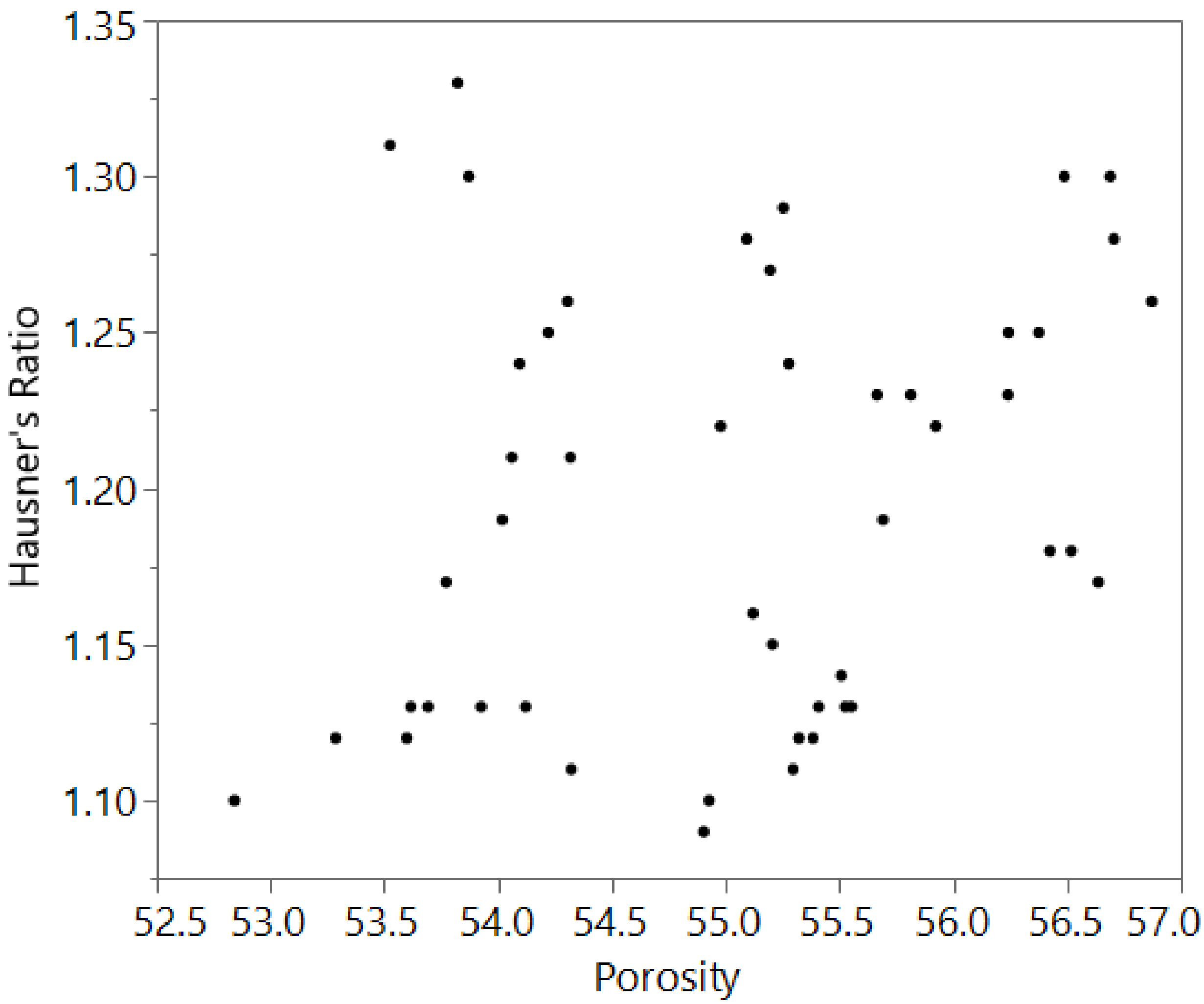


Figure 4.23. Relationship of Hausner's Ratio with porosity at 25°C

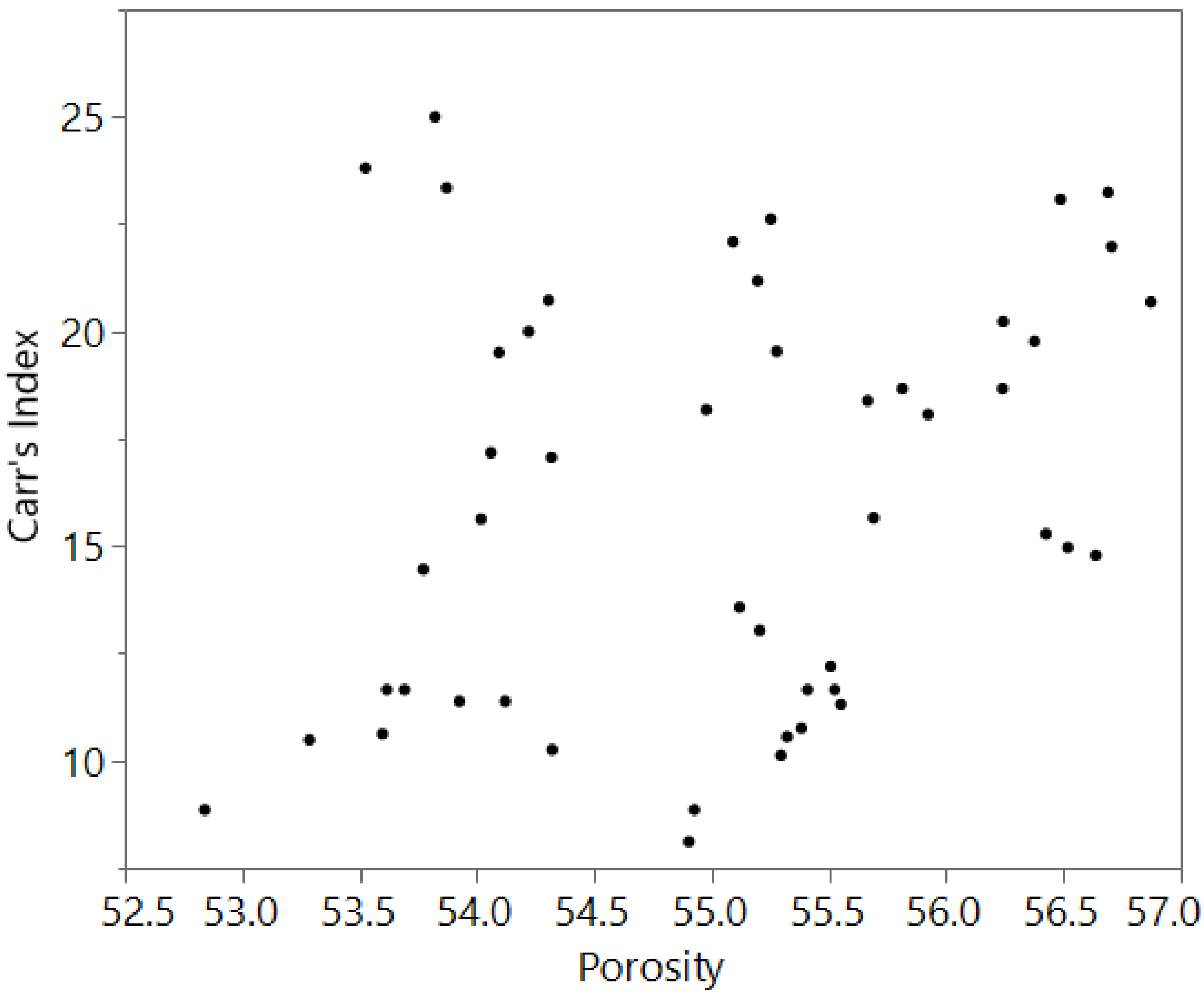


Figure 4.24. Relationship of Carr's Index with porosity at 25°C

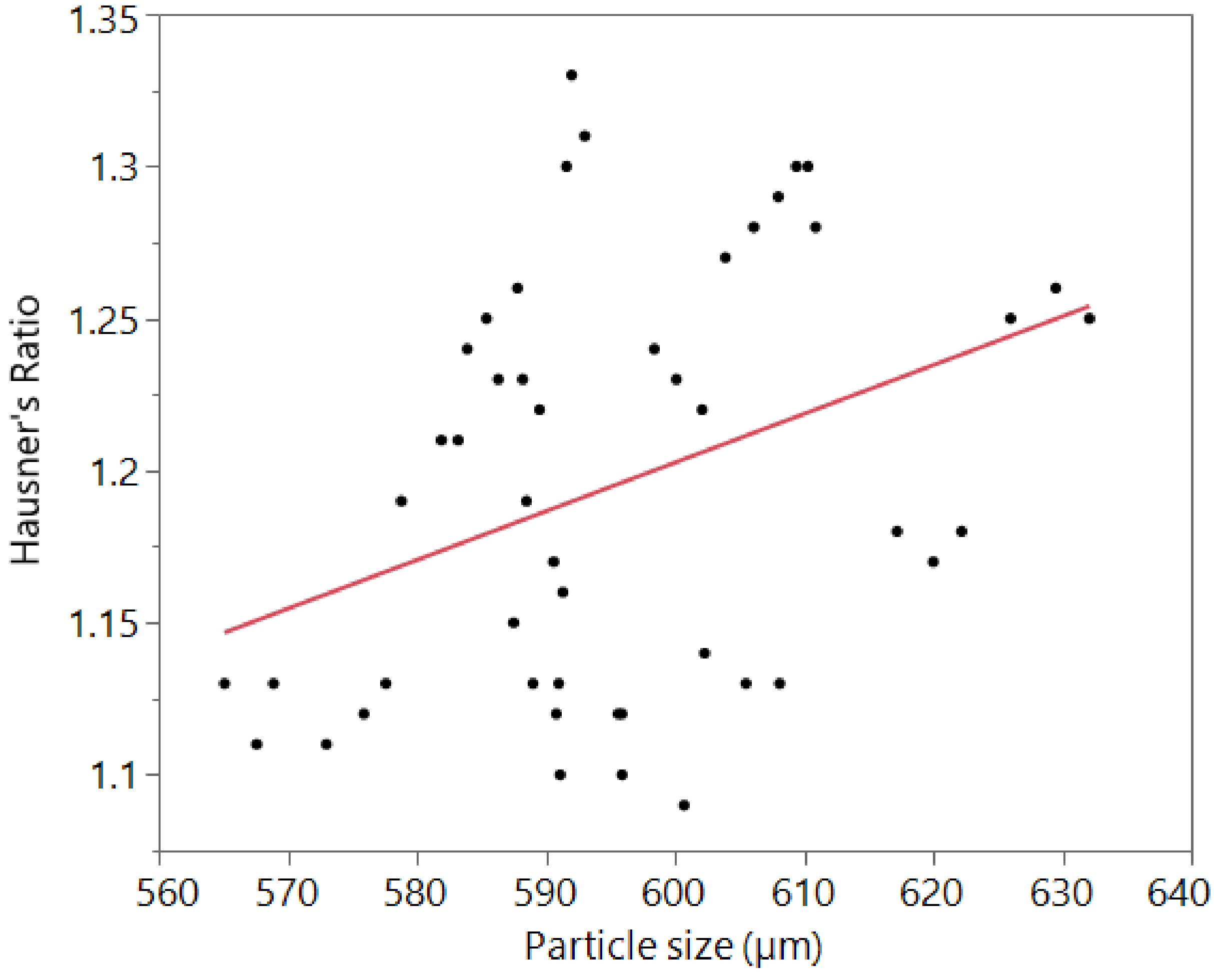


Figure 4.25. Relationship of Hausner's Ratio with particle size at 25°C

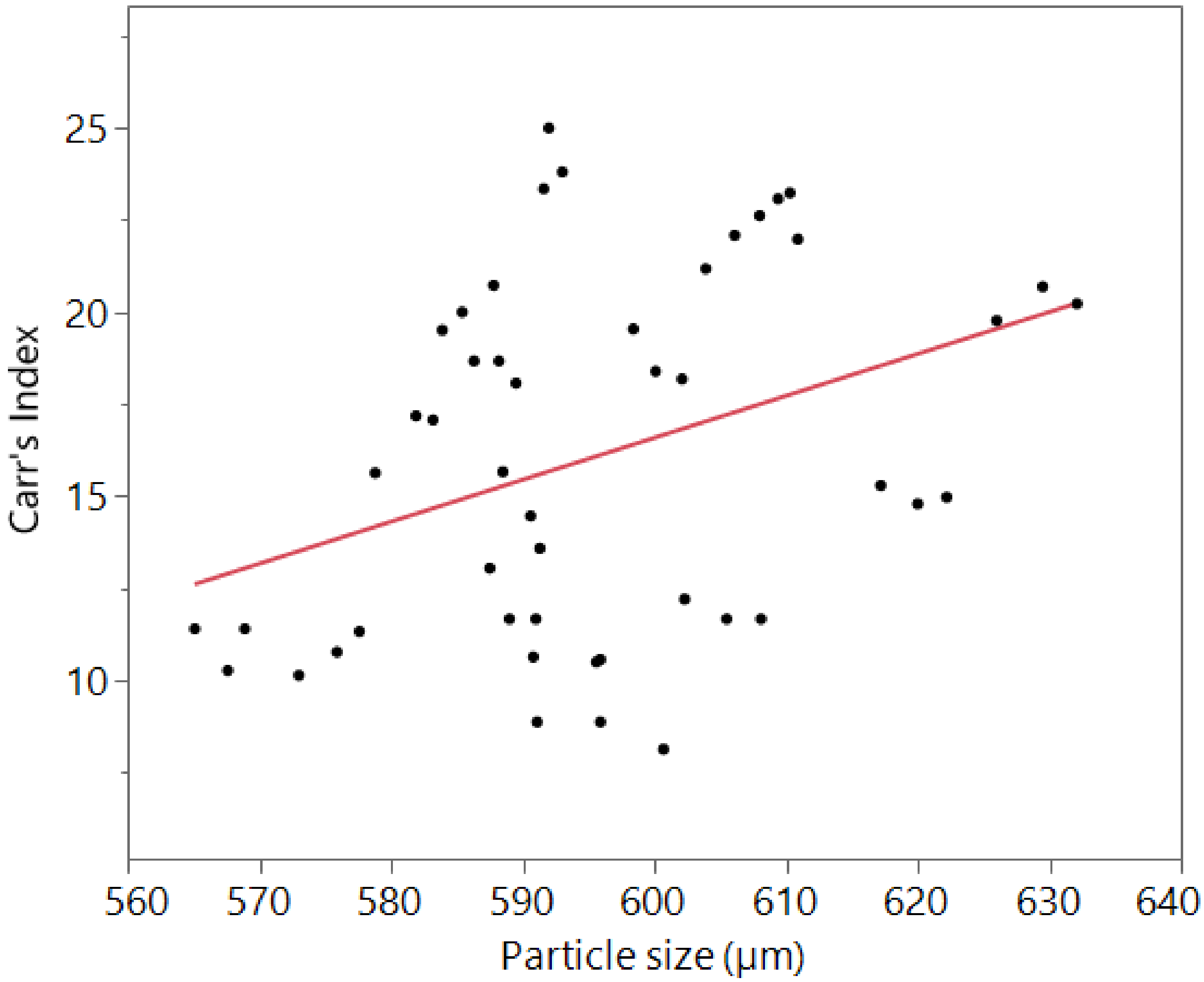


Figure 4.26. Relationship of Carr's Index with particle size at 25°C

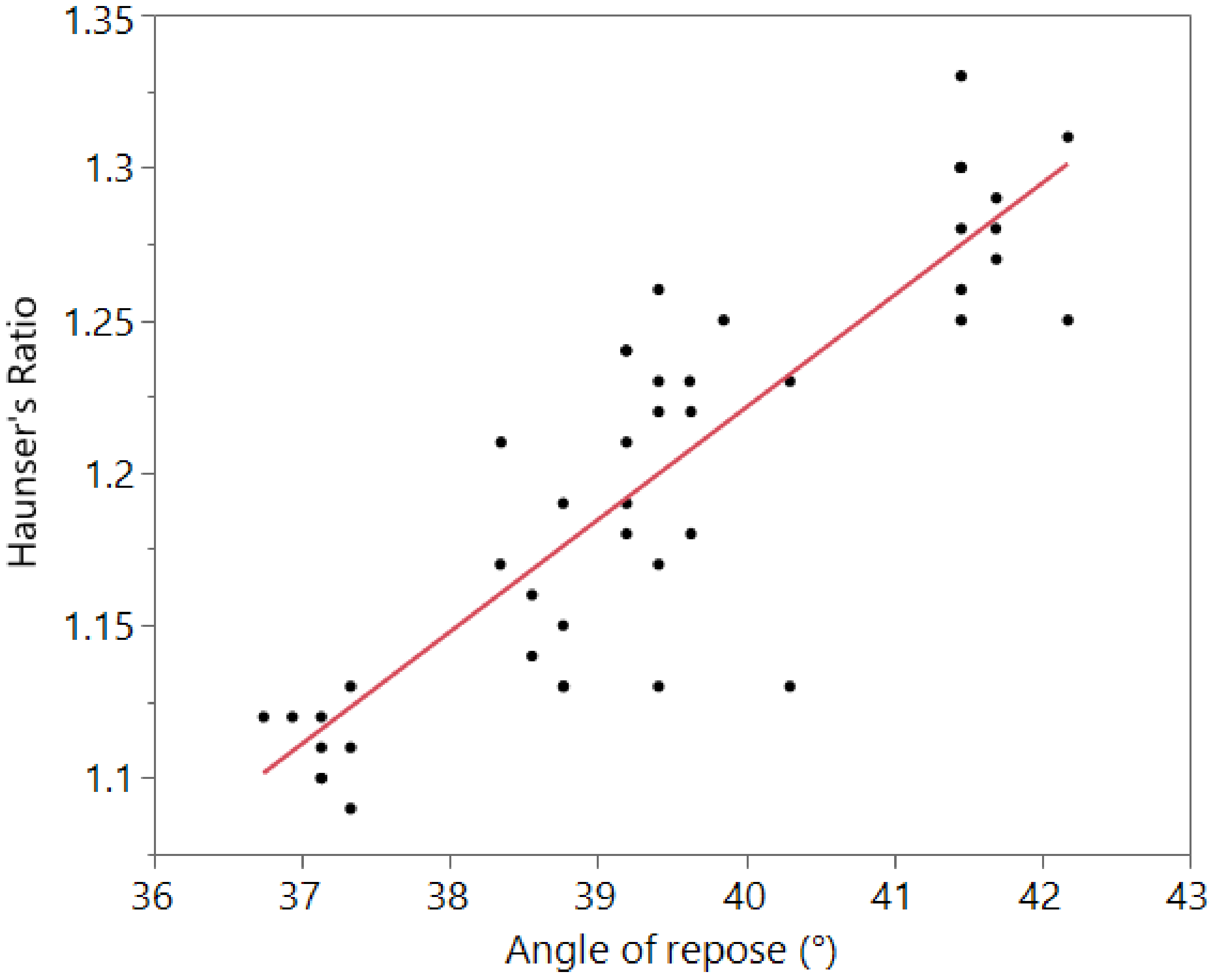


Figure 4.27. Relationship of Hausner's Ratio with angle of repose at 25°C

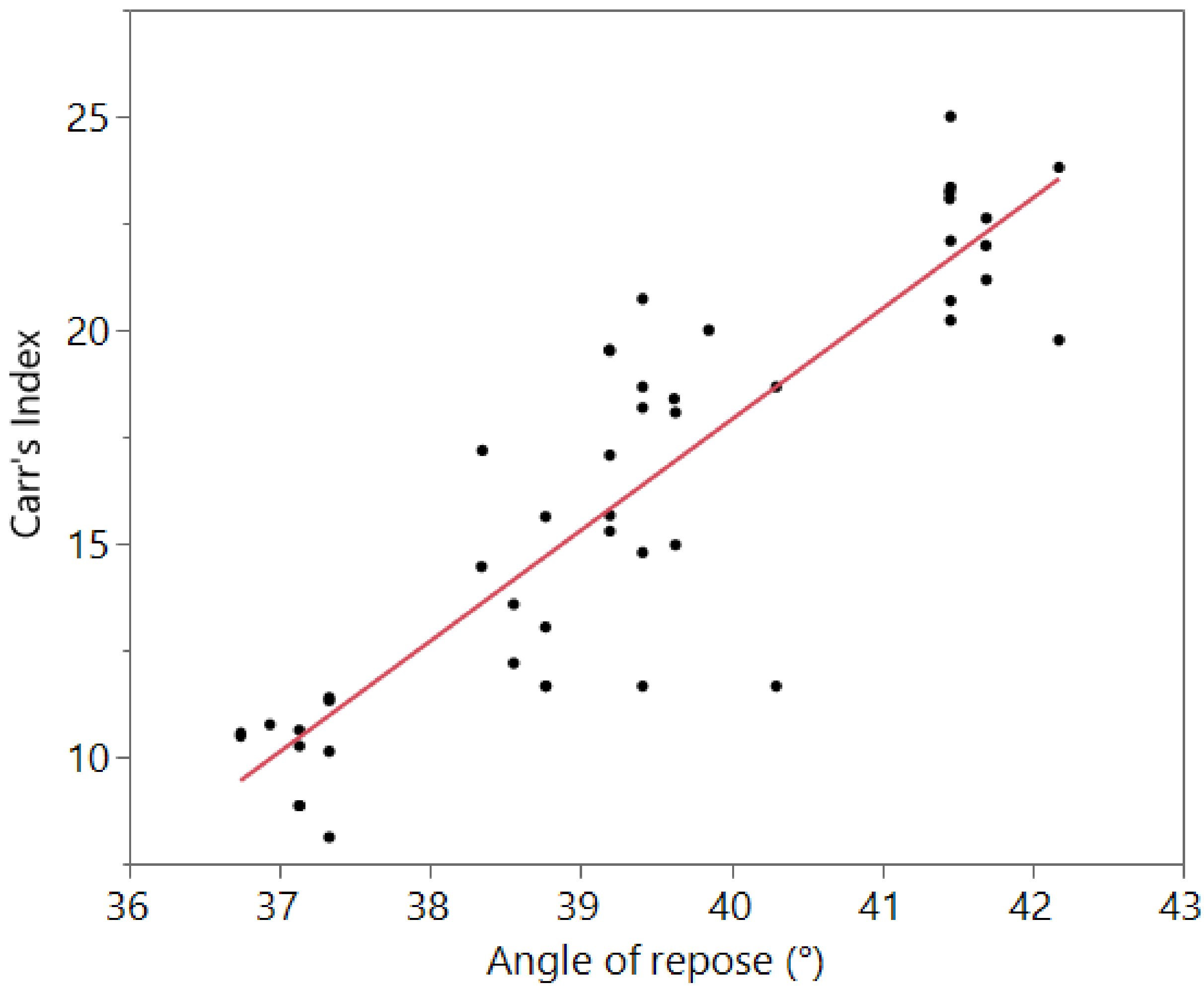


Figure 4.28. Relationship of Carr's Index with angle of repose at 25°C

4.3.2. Relationship of porosity with particle size and angle of repose

The relationship of porosity with particle size followed a positive linear trend (Figure 4.29). Increase in the particle size lead to increased porosity which due to the reason the larger particles occupied larger volume with increased distance between each particle creating voids. From table 4.19, the R-squared value for porosity and particle size is 0.38 with correlation 0.61 signifying a positive linear correlation. The R-squared value for porosity and angle of repose is 0.15 with correlation 0.39 signifying a weak positive correlation (Figure 4.30).

Table 4.19. Relationship of porosity with particle size and angle of repose.

		Particle size	**Angle of repose**
Porosity	$\mathbf{R^2}$	0.38	0.15
	Correlation	0.61	0.39

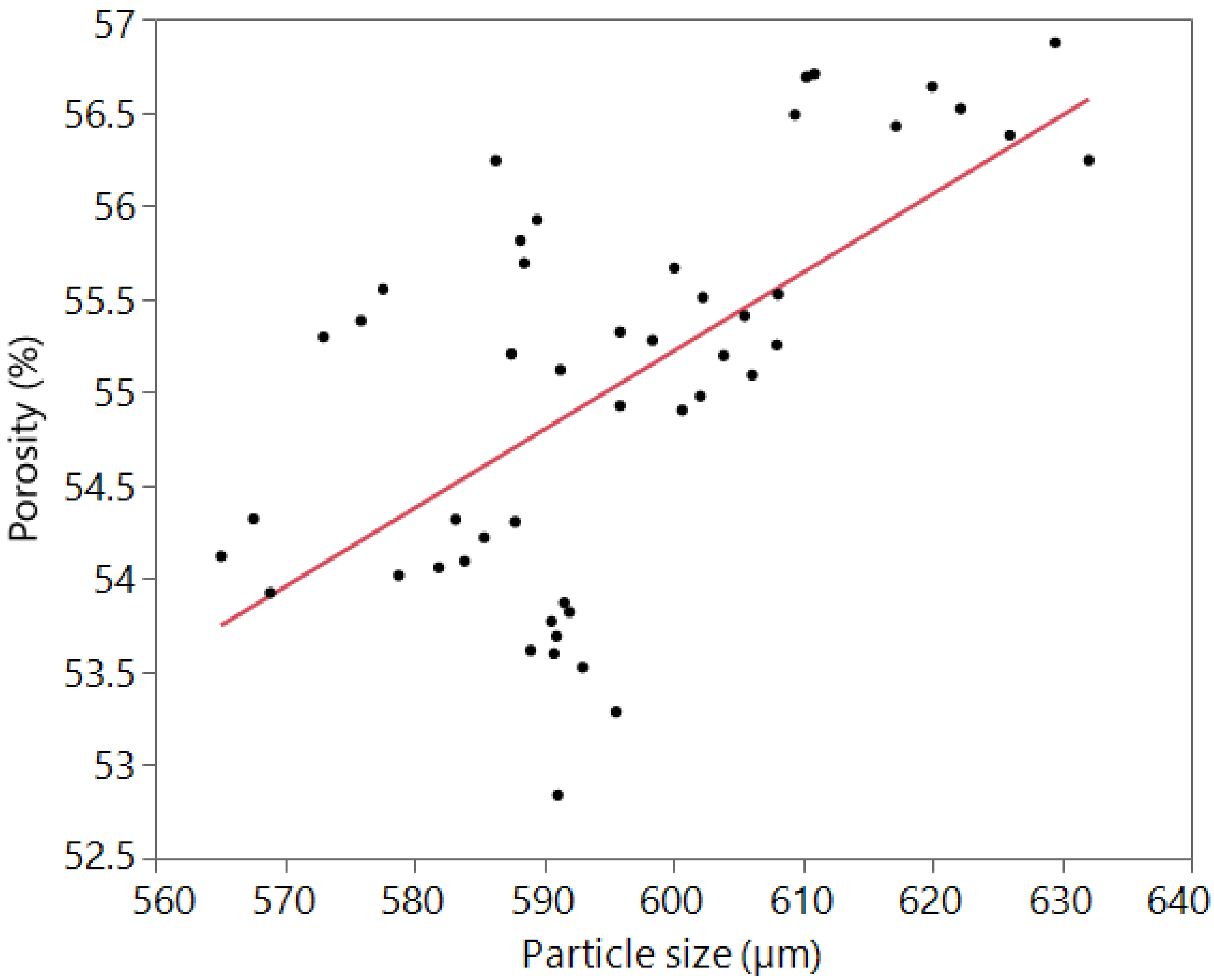


Figure 4.29. Relationship of Porosity with particle size at 25°C

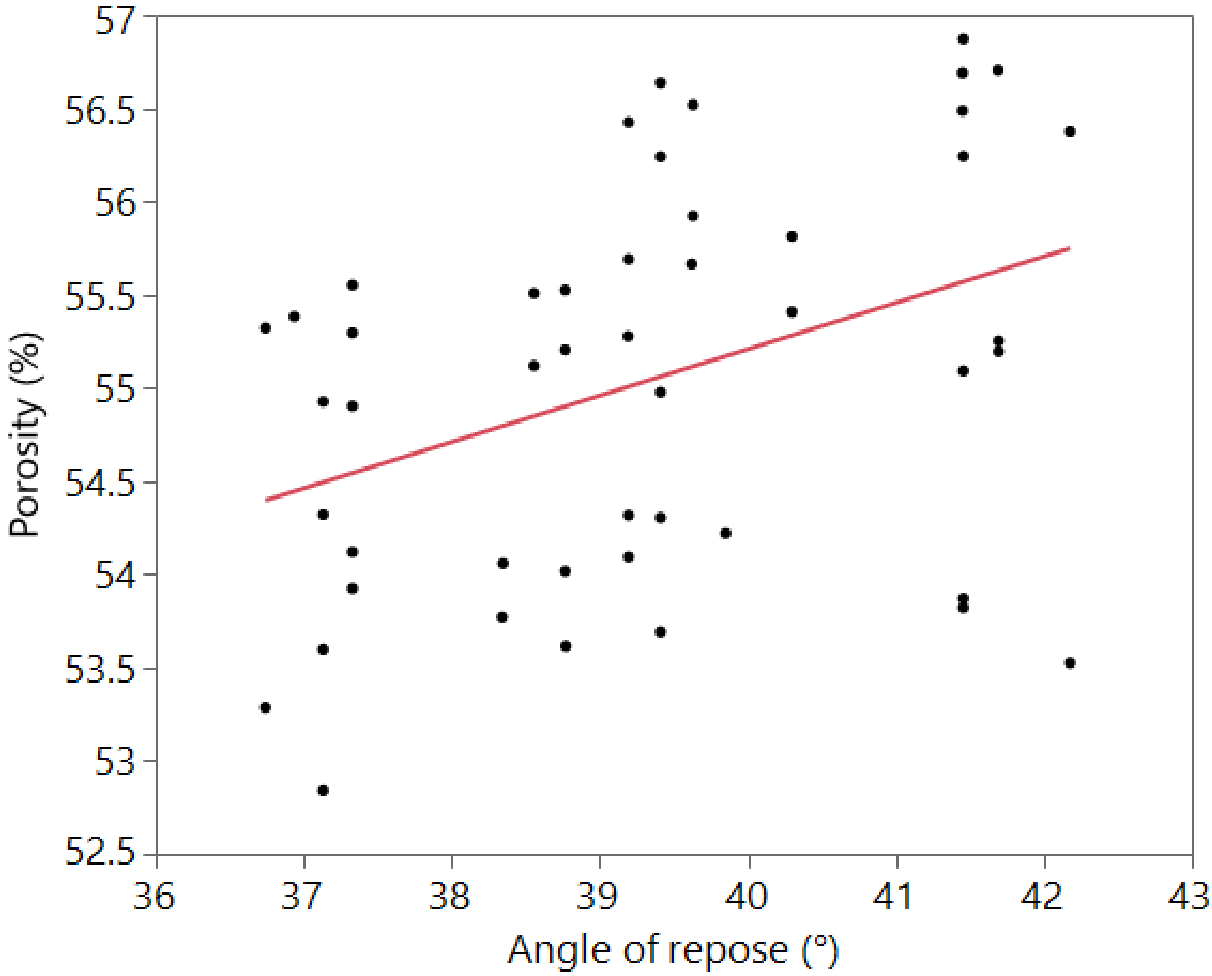


Figure 4.30. Relationship of Porosity with angle of repose at 25°C

4.3.3. Relationship of particle size with angle of repose

The angle of repose increased with increasing particle size diameter indicating that the powder flowability decreased with increasing particle size (Figure 4.31). However, the angle of repose was not influenced significantly ($p < 0.05$) by the particle size. From table 4.20, the R-squared value suggests that particle size cannot be used to predict the angle of repose and the two quantities do not have a strong correlation between them.

Table 4.20. Relationship of particle size with angle of repose.

		Angle of repose
Particle size	$\mathbf{R^2}$	0.35
	Correlation	0.59

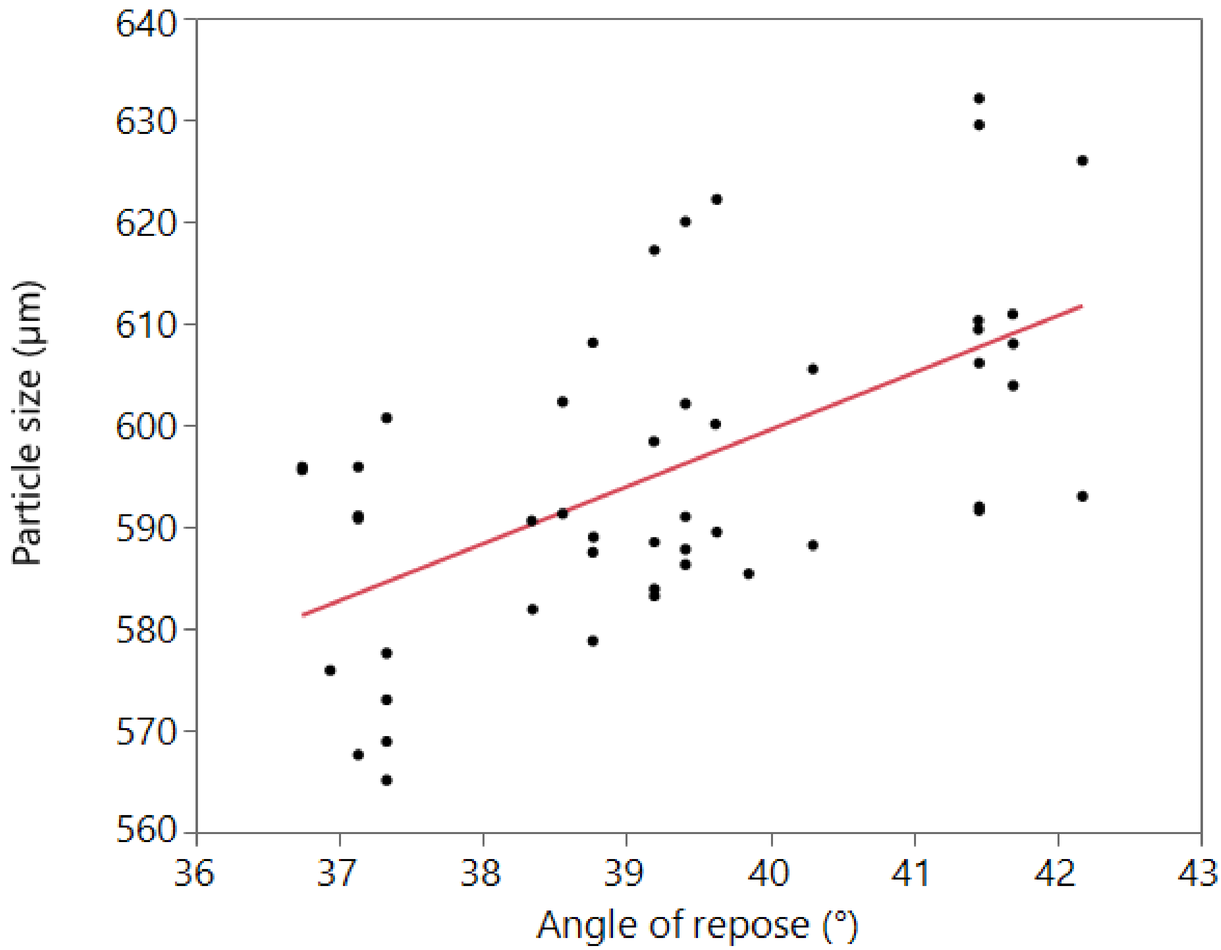


Figure 4.31. Relationship of particle size with angle of repose at 25°C

4.3.4. Relationship of flow index with angle of internal friction and angle of wall friction

From table 4.21, the angle of internal friction had a correlation coefficient of -0.02 with flow index. The values of flow index cannot be determined using the angle of internal friction (Figure 4.32), which was signified by the weak coefficient of correlation. Decrease in the angle of internal friction is a sign of increase in the flowability of the powders but for cornmeal, this was overpowered by other factors resulting in poorer flowability with decreasing angle of internal friction.

The angle of wall friction had a correlation coefficient of -0.73 with flow index. This signifies that the two have a strong negative linear relationship (Figure 4.33). With increasing wall friction, the flow index decreased which signifies that the flowability decreased. The flow function can be estimated based on the following expression:

$$ff_c = 10.78\text{-}0.43\times\varphi_w \tag{4.14}$$

where ff_c is the flow index, φ_w is the angle of wall friction

Table 4.21. Relationship of flow index with angle of internal friction and angle of wall friction.

		Angle of internal friction	**Angle of wall friction**
Flow index (*ff*$_c$)	**R^2**	0.00	0.54
	Correlation	-0.02	-0.73

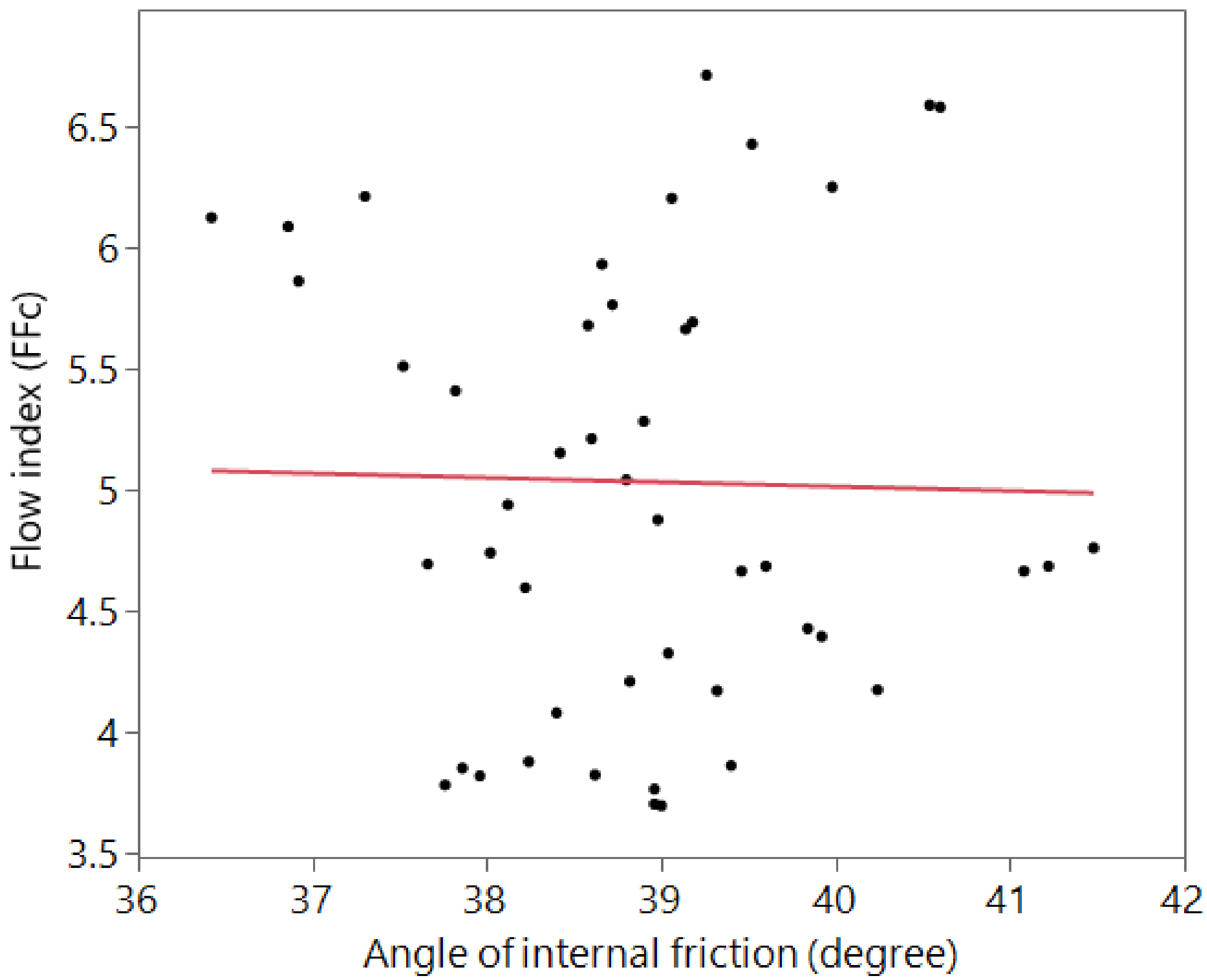


Figure 4.32. Relationship of angle of internal friction with flow index at 25°C

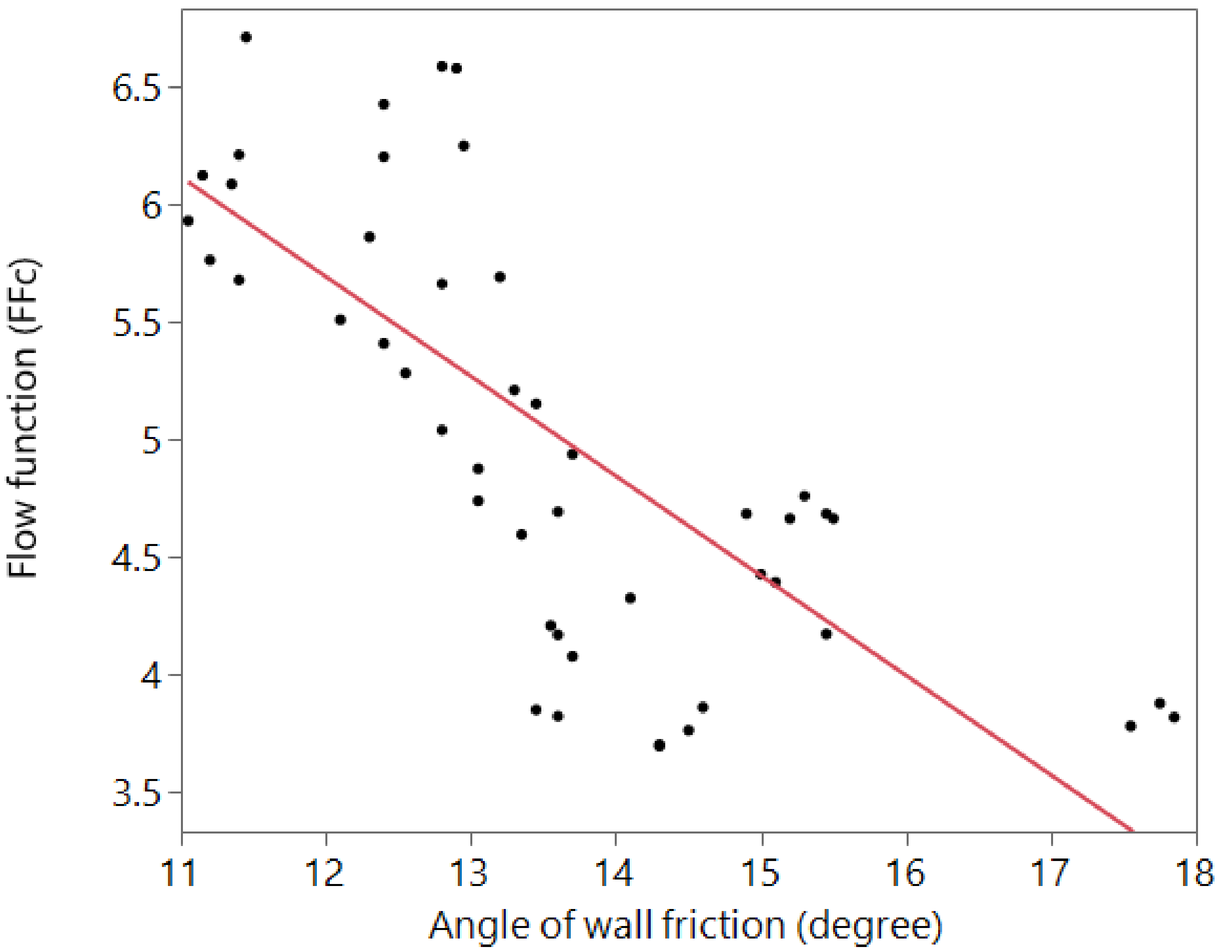


Figure 4.33. Relationship of angle of wall friction with flow index at 25°C

4.3.5. Relationship of flow index with Hausner's Ratio/Carr's Index, porosity, particle size, and angle of repose

The physical properties of cornmeal powder do have a major impact on its flowability. Flow properties can be determined using a shear tester, but this procedure is time consuming and expensive whereas determining physical properties such as bulk and tapped density of powders are easy to measure. Therefore, a correlation of Hausner's ratio (HR), Carr's Index (CI), porosity, particle size, and angle of repose with the flow index (ff_c) was established for cornmeal powder samples with varying moisture levels and calcium stearate concentration. The Hausner's Ratio or Carr's Index was selected to relate to the flow index of cornmeal powder as it was found to be the most significant ($p<0.05$).

Hausner's ratio was found to yield the best fit in relation to the flow index. Flow index gives an accurate measure of the flowability of the powder and was considered to be the most significant measure for characterizing flowability. There is a strong correlation between the flow index and Hausner's ratio which can be seen in table 4.22. The data obtained in this study was fitted using a power law function (Figure 4.34) which resulted in the following equation ($R^2 = 0.86$):

$$ff_c = 8.54\times(\text{HR})^{-3.07} \qquad (4.15)$$

$$ff_c = 21.61\times(\text{CI})^{-0.54} \qquad (4.16)$$

where ff_c is the flow index, HR is the Hausner's Ratio, and CI is the Carr's Index

A similar model was proposed by Saw *et al.* (2015) for lactose powder, sand, and refractory dust. With the increase in Hausner's Ratio, the flowability of cornmeal powder decreased significantly ($p<0.05$). The trend of flow index with respect to Carr's Index was similar. As the value of Hausner's Ratio increased, the value of flow index decreased nonlinearly.

The relationship between porosity and flow index was insignificant (Figure 4.35). Figure 4.35 shows that there is no correlation between porosity and flow index. Powder porosity is not a reliable parameter to predict the flow index values for cornmeal powder at varying moisture contents and calcium stearate concentrations. Porosity of cornmeal powder is influenced by the particle density and bulk density.

The relationship between flow index and angle of repose was determined and is represented in Figure 4.36. The angle of repose can be determined experimentally with ease but the measurement is not very consistent as it contains many experimental errors and any relation with flow index cannot be accurately established. The R^2 value for the fit was 0.80 and the relation was given by:

$$ff_c = 1.39\times10^7 (\propto)^{-4.04} \quad (4.17)$$

where ff_c is the flow index and $\propto$ is the angle of repose

Table 4.22. Relationship of Hausner's Ratio and Carr's Index with porosity, particle size, and angle of repose.

		Hausner's Ratio/ Carr's Index	Porosity	Angle of repose
Flow index (ff_c)	**R^2**	0.86	-	0.80
	Correlation	0.91	0.88	0.88

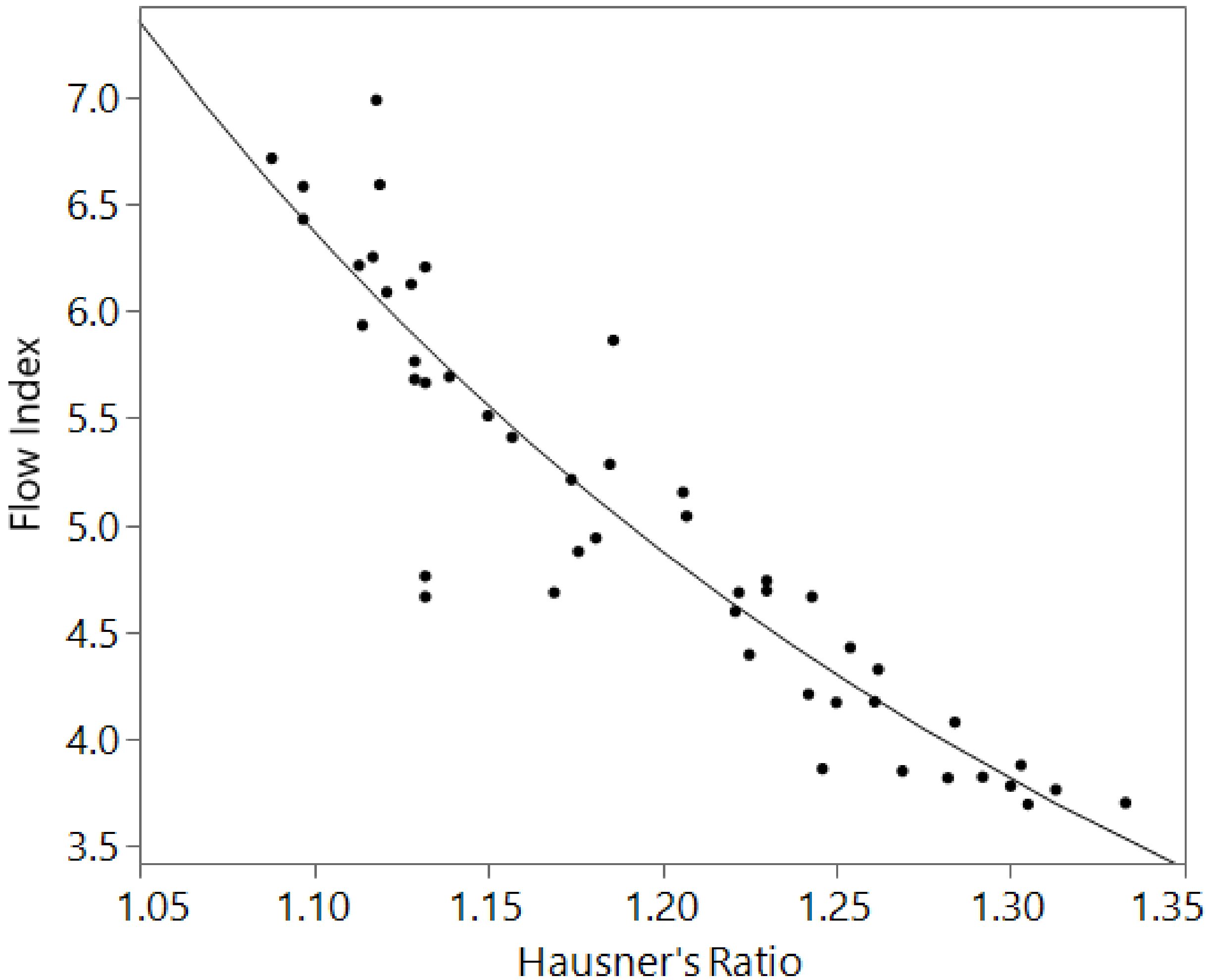


Figure 4.34. Variation of flow index of cornmeal powder with Hausner's Ratio. The line represents the prediction model (Eq. 4.12)

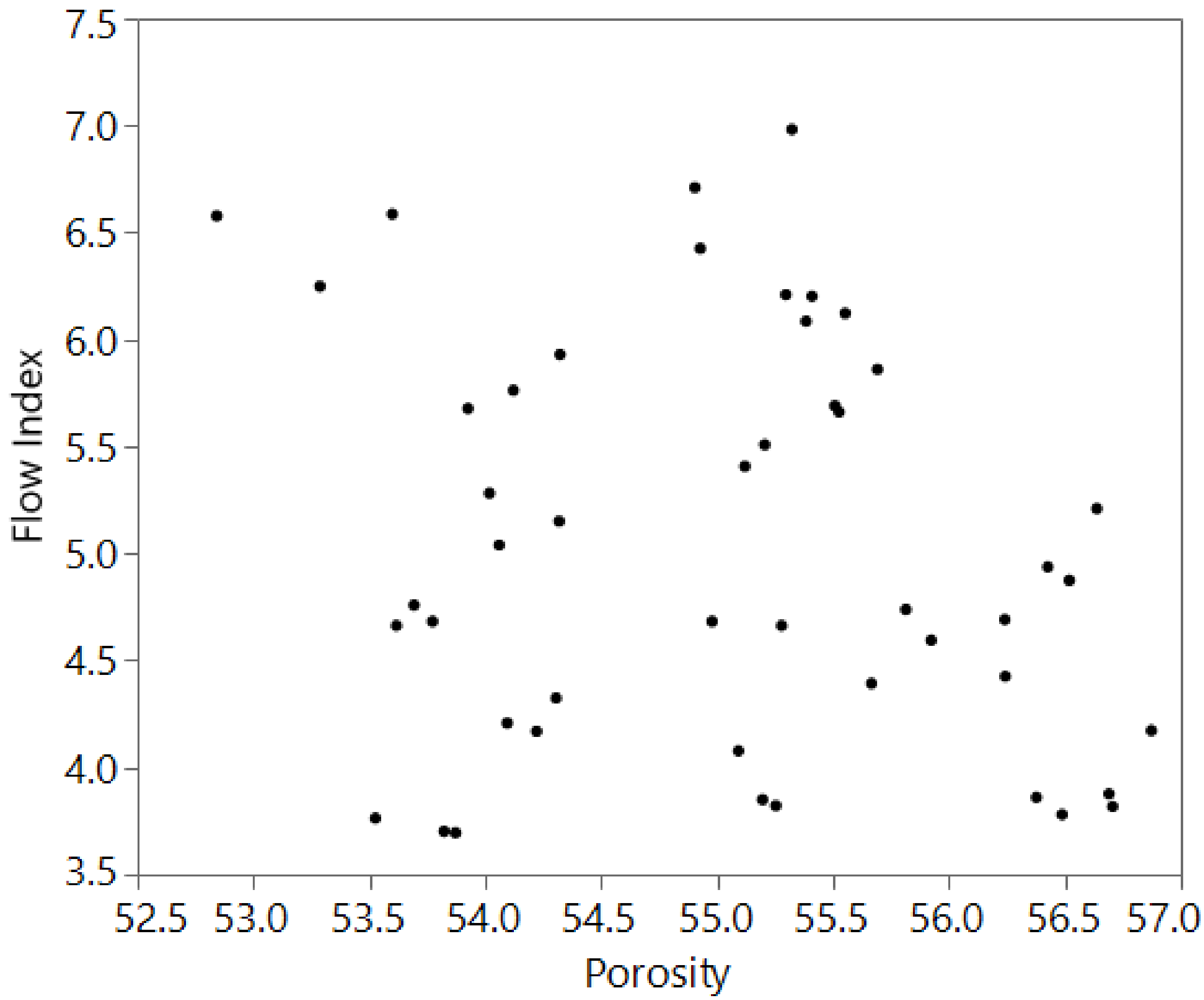


Figure 4.35. Variation of flow index of cornmeal powder with Hausner's Ratio

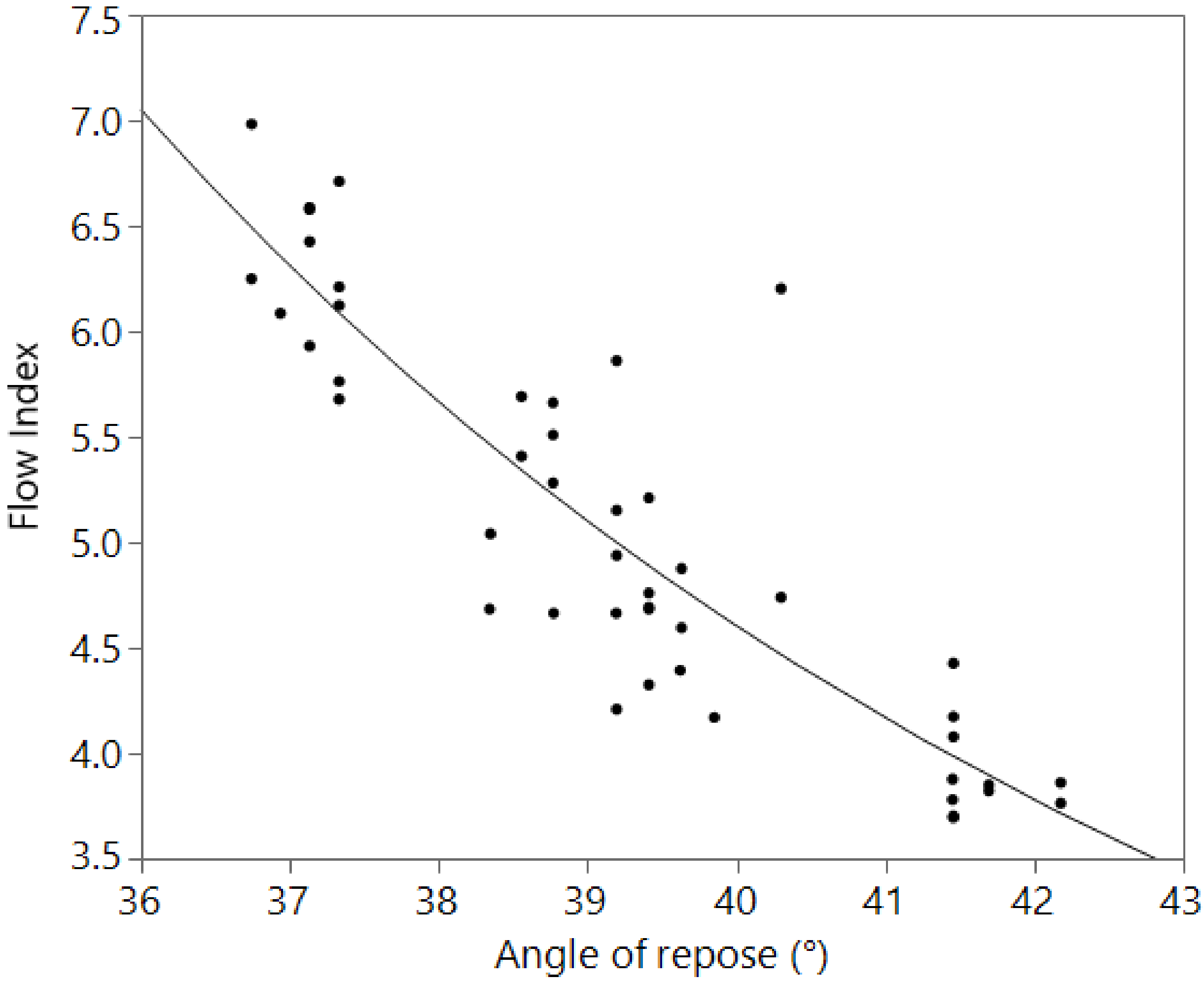


Figure 4.36. Variation of flow index of cornmeal powder with angle of repose

4.3.6. Relationship of flow index with hygroscopicity of the samples

There was a positive weak correlation between the flow index and hygroscopicity of the samples with a correlation coefficient of 0.38. The hygroscopicity was the least for 1.00% wt/wt calcium stearate concentration whereas the best flow behavior was for 0.50% wt/wt calcium stearate. Even though the amount of moisture absorbed by the sample with 1.00% wt/wt calcium stearate was the least, the flow behavior must have been impacted by the concentration of the conditioner.

CHAPTER V

CONCLUSIONS

5.1. Conclusions

In this study, the effect of moisture content and concentration of calcium stearate on the flow behavior of cornmeal powder was investigated and quantified. Different physical and flow properties were measured to characterize the flow behavior of the powders.

- Bulk density decreased significantly ($p<0.05$) with increasing moisture content which affected the flow behavior by resisting flow.
- With increase in moisture content, the particle size increased but this increase in size did not aide the flow as moisture within the sample over powered the effect of large powder particles known to enhance flowability.
- Tapped density of the samples increased with increasing moisture content as the particles started rearranging themselves and creating an efficient packing fraction.
- Hausner's ratio and Carr's Index were lowest at 0.50% wt/wt calcium stearate and 10.0% moisture content (w.b.) indicating excellent flow. Thus, the flow behavior was enhanced by the addition of 0.50% wt/wt of calcium stearate to the cornmeal sample. Beyond this concentration, the effect on flowability was not very significant.
- Particle density and porosity were not very significant in predicting the flow behavior. The values of porosity did not follow any specific trend and were difficult to relate to the flow behavior of cornmeal powder. The reason for this is the change in particle density, which was used to calculate the porosity. The particle density decreased with increasing moisture

but its impact on the sample was reverse as. The flowability decreased with increase in moisture content.

- Particle size increased with increasing moisture content and was the highest for cornmeal powder samples at 0.50% wt/wt calcium stearate. This relates well with the flow behavior predicted by Hausner's Ratio and Carr's Index. Higher particle size relates to better flowability.
- Angle of repose also suggested that the best flowability was achieved at 10.0% moisture content and it decreased with increasing moisture content. The value of angle of repose at 10.0% w.b. moisture level was found to be 37.00 ± 0.22, which depicted good flow behavior with a little or no cohesiveness.
- Flow function of the samples resulted in 0.50% wt/wt calcium stearate and 10.0% moisture content giving the best flow index. The increase in the liquid bridges formed in moist powders was alleviated by addition of calcium stearate, which acted as a lubricant to come extent. Increase in the concentration of calcium stearate lead to increased Van der Wall forces and therefore did not enhance the flow after a certain concentration (0.50% wt/wt). The angle of internal friction and wall decreased due to the decrease in the friction between particles as the size increased. It is known that when hygroscopic powders are exposed to a high RH, they cake and presence of anticaking agents does not alleviate this issue after a certain point.
- Moisture isotherms for all the samples were type II isotherms. Adding calcium stearate did not affect the EMC of the tested samples. The samples with 0.50% wt/wt calcium stearate absorbed the lowest moisture in comparison to other samples.

- For the samples investigated, Peleg model provided the best fit of the isotherms. Guggenheim-Anderson-de Boer (GAB), Ferro-Fontan, Peleg, and Oswin models also provided a good fit of the experimental data.
- Sufficient correlation was not found for all the physical properties, but Hausner's Ratio and Carr's Index were able to relate to the flow index. This analysis provides an easier means to predict the flowability of cornmeal based on the bulk and tapped densities.

5.2. Recommendations for further study

Results from this study provided good quantitative information of physical and flow properties of cornmeal powder at room temperature. However, the effect of other factors on the flowability of powders such as shape of the particles, time of storage, temperature, and relative humidity are still needed to be studied to thoroughly understand the flow behavior of cornmeal powder.

Particle shape is one of the factors that may influence the flowability of the cornmeal powder which can be a topic of investigation in the subsequent studies. Flow behavior that could not be explained based on the properties tested in this study might be due to the shape of the particles. Thus, accurate characterization of the shape of the powder particles would add to the current knowledge.

Another recommendation is to test the flow behavior of cornmeal on different wall materials. Since this study was based on storage of cornmeal powder, wall friction has an important role to play and materials that provide minimum resistant to the flow of cornmeal powder would aide in better storage of the powder.

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