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STUDIES OF DRY-ROASTED AND AIR-CLASSIFIED NAVY BEAN FLOUR FRACTIONS: PHYSICOCHEMICAL CHARACTERISTICS, STORAGE STABILITY, AND RHEOLOGICAL PROPERTIES

presented by

James J. Lee

has been accepted towards fulfillment
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STUDIES OF DRY-ROASTED AND AIR-CLASSIFIED NAVY BEAN FLOUR FRACTIONS: PHYSICOCHEMICAL CHARACTERISTICS, STORAGE STABILITY, AND RHEOLOGICAL PROPERTIES

By

James J. Lee

A DISSERTATION

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ABSTRACT

STUDIES OF DRY-ROASTED AND AIR-CLASSIFIED NAVY BEAN FLOUR FRACTIONS: PHYSICOCHEMICAL CHARACTERISTICS, STORAGE STABILITY, AND RHEOLOGICAL PROPERTIES

By

James J. Lee

Navy beans (*Phaseolus vulgaris*) were dry-roasted in a particle-to-particle heat exchanger under various roasting conditions, dehulled by air aspiration, pin-milled, and air-classified to yield whole, hull, high protein, and high starch flour fractions. Evaluation of these flours was conducted in three studies.

Compositional differences were demonstrated among all flour fractions. Stachyose was the major oligosaccharide in all fractions and was the highest in the protein fraction. Substituting 10% bean flours for wheat changed water absorption and dough stability for all fractions. Pasting characteristics of whole flour and high starch flours were demonstrated to be controlled swelling at high temperature.

Flour fractions from four roasting treatments were stored under eight water activity levels (a_w's). High roasting time/temperature conditions resulted in decreased equilibrium moisture. After two months storage, flours in a_w above 0.75 were moldy. Flours stored in increased a_w showed increased browning with concurrent decrease of protein solubility and glucose content. Flours stored up to 24 months with 6% and 9% moisture at 20°C or with 6% moisture at 37.7°C retained good quality.

Gelatinization and rheological properties of purified starch pastes (6%, 8%, 10%, and 12%) were evaluated using a computer assisted Haake Viscometer. Pastes were stirred at a constant shear rate of 50 rpm at 75°C, 85°C, and 95°C for up to 60 min. Activation energy of starch gelatinization was estimated to be 14.5 Kcal/g mole.

Various swelling responses of starch during cooking were demonstrated. Maximum final viscosity values were obtained at 85°C for all starch concentrations except a maximum at 95°C for 6%. Thixotropic breakdown was observed at 10% and 12% concentration during initial shearing at 85°C and 95°C.

Flow behavior, retrogradation tendency, and stability of the hot and cooled (50°C) pastes were determined after cooking. The power law, Herschel-Bulkley, and Casson models characterized the paste flow. Gelatinized pastes exhibited shear thinning behavior; their flow curves best fit the Herschel-Bulkley model. Yield stress, consistency index, and flow behavior index were concentration and temperature dependent. Significant paste rheological property changes occurred at starch concentrations above 10% for 75°C and above 8% to 10% for 85°C and 95°C.

To my loving wife, Shu-wei

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I am very grateful to Mrs. Uebersax, who is so special to my family, for her loving care and constant inspiration, and to my fellow graduate students in Lab 128 for their companionship and suggestions during the period the research was conducted.

Finally, I am deeply indebted to my parents, from whom I have learned to treasure the desire for unending knowledge.

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a_w	Water activity
CV	Coefficient of variation
D	Diameter of impellers
db	Dry weight basis
EMC	Equilibrium moisture content
ERH	Equilibrium relative humidity
g	Gravitational acceleration
g_c	Dimensional constant relating force and mass (1 g.cm/dyne.sec^2)
h	Submerged height
K	Consistency index (computed from the Power Law or the Herschel-Bulkley model)
K_c	Consistency index (computed from the Casson model)
K_o^2	Casson yield stress
L	Distance from bottom of cup to bottom of bob
M	Torque
M_o	Initial torque
M_m	Maximum torque
m	Rheological constant: n-1
N	Mixer speed
n	Flow behavior index
P	Power required for mixing
Q	Exponent empirically related to Re for given set of shape factors of the mixer
r^2	Square of the Correlation Coefficient

R_b	Bob radius
R_c	Cup radius
Re	Reynolds number
SS(b)	Sum-of-squares function
t	Time
wb	Wet weight basis
ρ	Density
ω	Angular velocity
ν	Velocity
θ	Time
γ	Radial distance measured from center, or radial coordinate
ϕ	Angular coordinate
z	Axial coordinate
Ω	Angular velocity
η	Newtonian viscosity
η_{app}	Apparent viscosity
τ	Shear stress
τ_y	Yield stress through direct measurement
τ_o	Yield stress through curve fitting
τ_c	Shear stress at cup wall
τ_b	Shear stress at bob wall
$\dot{\gamma}$	Shear rate
$\dot{\gamma}_b$	Shear rate at the bob

INTRODUCTION

Michigan grows about 33% of the colored beans, 70% of the navy beans, and 30% of the total dry edible beans produced in the United States. Approximately 10,000 farmers in Michigan raise dry edible beans as a cash crop and over half a million acres are planted in this crop each year (Anon., 1979). These dry edible beans provide significant levels of protein and other essential nutrients to the diets of people from both developed and subsistant agriculture. Regardless of the superior nutrition provided by dry beans, their consumption has declined from about 7.6 lb per capita in 1962 to 4.1 lb per capita in 1981.

Dry beans traditionally have been prepared by soaking and cooking in the home or consumed as commercially processed canned beans. Whole beans require soaking and cooking to ensure uniform expansion of the seed coat and hydration of the cotyledon matrix. Long cooking times to achieve satisfactory palatability have impeded further utilization of dry beans. The use of dry edible beans could be readily expanded if they were available in the form of a shelf-stable flour.

Bean flours have been prepared by soaking and cooking beans in water and steam followed by high temperature dehydration over drum driers (Bakker-Arkema et al., 1967). Due to the high carbohydrate and high protein contents of legume seeds, research has oriented to the production of high starch and high protein concentrates using solvent extraction techniques either in pilot or commercial scale. The

properties and functionality of these concentrates have been evaluated (Schoch and Maywald, 1968; Sathe and Salunkhe, 1981c; Chang and Satterlee, 1979; Vose, 1980). Although this wet processing method results in high yields and high percentage values of protein and starch in their concentrates, it is energy intensive, generates large quantities of waste effluent, and results in a decline in nutritive value due to leaching.

Milling and fractionation of legumes to produce flour products have received increased interest in recent years. Milled products such as whole flour and air-classified high protein and high starch fractions from beans have demonstrated high nutrient retention and provide increased versatility and improved utilization of beans. A number of studies on milling of legume flours and incorporation of flour into food products have been reported. Field peas have been successfully milled into whole flour and air-classified into high protein and high starch concentrates (Vose et al., 1976). Yield and compositional data of high protein and high starch concentrates of various legume seeds obtained through air-classification were reported (Patel et al., 1980; Tyler et al., 1981; Sahasrabudhe et al., 1981).

It was noted, however, that legume seeds contain antinutritional factors such as trypsin inhibitors and lectins which will exert undesirable effects on their nutritive value if they are not inactivated (Puztai, 1967; Jaffe, 1975). In a recent study (Aguilera et al., 1982b), navy beans were dry roasted in a particle-to-particle heat exchanger prior to milling and air-classification to maximize the nutritive potential of the whole, hull, high protein, and high starch fractions.

The utilization of bean flour of varying extractions from untreated and dry-roasted split navy beans has been investigated for bread making

(D'Appolonia, 1978). Functional properties of starch flour prepared from various legumes were studied by Schoch and Maywald (1968) and Naivikul and D'Appolonia (1979). Rheological properties of dough and baking quality of bread as affected by the addition of navy bean flour and protein concentrate were studied (Sathe et al., 1981b). Cereal brans have been incorporated into bread, cakes, and cookies to produce baked products with high fiber contents (Pomeranz et al., 1977; Rajchel et al., 1975; Shafer and Zabik, 1978; Vratanina and Zabik, 1978). Research conducted by DeFouw et al. (1982) concluded that navy bean hulls were an acceptable source of dietary fiber in spice-flavored layer cakes. The physicochemical characteristics of dry-roasted navy bean flour fractions, however, have not yet been thoroughly investigated.

Quality change of dry bean flours and their fractions during storage has been a major concern. Earlier work has shown certain quality changes in dry foods including protein solubility, browning reactions, and lipid oxidation (Henry and Kon, 1950; Buchanan, 1969a,b; Koch, 1962; Matsushita, 1975).

The significance of water activity to the deterioration of the quality and nutritive value of stored dry skim milk was investigated by Henry and Kon (1948) and Lea and White (1948). Counter (1969) evaluated the effect of processing instant bean powder on the deterioration rate of quality parameters such as lipid content, color, protein solubility, and reducing sugar content. Love (1975) studied the effect of storage atmosphere and water activity on lipid and protein content of navy bean powder under accelerated conditions at 37°C. The stability of pea flour products was evaluated by Sumner et al. (1979) during a one year period at various moisture and temperature levels. No information has been found pertinent to the effect of water activity on the quality

characteristics of air-classified navy bean flours during storage.

High starch flour comprises about 50% or more of the total yield after air-classification, with starch being the major portion of the starch flour. Starch has been used in the food industry as a thickening agent in products such as gravies, sauces, puddings, and pie fillings to achieve the desired consistency. Starches are also used as diluents in chemical and pharmaceutical industries, as carriers in cosmetics and tablets, and as binders in the paper industry. The rheological measurements of starch or starch containing products are frequently used for quality control and some engineering applications.

It is known that the starch granules will swell in the presence of water as the temperature of the starch paste is raised to the gelatinization range and the granules continue to swell if sufficient water and heat are supplied. At this stage the granules are very susceptible to thermal and mechanical breakdown, thereby decreasing the paste viscosity. Rheological study of the starch pastes, therefore, becomes very difficult due to the continuous change of the paste property.

The gelatinization properties and pasting characteristics of various starches have been investigated extensively using empirical struments such as the Brabender Viscoamylograph (Sathe and Salunkhe, 1981a,b; Paton, 1981; Mazurs et al., 1957). Although this instrument is commonly used for testing starch properties, it can only run at low starch concentration and the viscosities are not given in absolute units due to its complicated geometry. Moreover, it can only provide single-point determinations and does not measure yield stress. Kempf and Kalender (1972) criticized the Viscoamylograph because it did not provide uniform heat transfer which resulted in non-uniform homogenization of the starch paste.

In contrast, the coaxial cylinder viscometer, such as Haake Rotovisco Viscometer, with a simple and well-defined geometry, readily provides flow curves and absolute viscosity units. This type of viscometer has been used recently for the rheological measurements of gelatinized starch pastes (Kempf and Kalender, 1972; Odigboh and Mohsenin, 1974, 1975; Evans and Haisman, 1979; Bagley and Christianson, 1982). These studies, however, did not provide basic information in the preparation of the starch pastes prior to measurements.

The present research was to evaluate some physicochemical properties of the dry roasted and air-classified navy bean flour fractions. Three independent studies were conducted in this work. The first study was to determine the chemical composition and to characterize the functional properties of dry-roasted navy bean flour fractions in order to evaluate the potential suitability of the flours for use in food systems. The second study was designed to assess the stability of flour fractions as affected by dry bean roasting treatment, water activity, initial moisture content, and temperature during short term and long term storage periods. The third study was conducted to evaluate the effect of cooking temperature and starch concentration on the gelatinization and rheological properties of purified navy bean starch pastes as measured with the Haake RV12 Viscometer. Flow behavior, retrogradation, and stability of the hot and cooled pastes were also examined.

REVIEW OF LITERATURE

Production of Bean Flours

Wet Processing

Processes for producing instant, precooked pea bean powder with good flavor and reconstitution characteristics were investigated by Bakker-Arkema et al. (1967). Pea beans were soaked at 210°F for 40 min and cooked for 90 min. The pureeing of the cooked beans was done on a pulper prior to drying either in the single or double drum drier. A later study by the same authors showed that the physical characteristics of instant legume powders of pea beans, peas, and lentils produced in a single drum drier were judged by consumer panels as highly acceptable (Bakker-Arkema et al., 1969).

Special methods were devised for separating the starch from legumes by Schoch and Maywald (1968). Mung beans, garbanzos, and dehulled split yellow peas were washed and steeped overnight under toluene at 50°C and wet milled in a Waring blender. The magma was screened through bolting cloth and washed with water. The residual pulp was again ground with water and rescreened. The combined starch suspension was then screened through nylon cloth and allowed to settle. The settled slurry was washed and screened several times and dried to pass through an 80-mesh sieve. For lentils, lima beans, and navy beans, seeds were steeped in water, ground, and screened as described above. The settled slurry was suspended in 0.2% NaOH and screened through 220-mesh nylon to remove

fine fiber, followed by flow down an inclined "table" to collect starch particles by gravity precipitation. This step was repeated several times and the final alkaline deposit of starch was suspended in water, neutralized with HCl and dried. Another extraction method was developed for separation of wrinkled-seeded peas in the same study by the above authors. Peas were steeped overnight in 0.3% NaOH, washed and ground with 0.2% NaOH in a Waring blender. The ground magma was screened through cloth and the suspension settled overnight. The screening and settling process was repeated several times and the final starch was neutralized, washed, and dried. These methods produced relatively low yields (ranging from 22% to 44%) of starches for various legume seeds.

The starch fractions of the germinated and ungerminated legumes were isolated by Morad et al. (1980). The legume flour was suspended and stirred in distilled water and the pH adjusted to 8.5 with 1 N NaOH. The extract was separated from the insoluble starch fraction by centrifugation. The starch was extracted again and washed three times with water followed by freeze-drying.

Sathe and Salunkhe (1981c) also employed the solvent extraction technique to isolate the Great Northern bean starch. Beans were ground to 20 mesh in a Fitz mill and the flour was extracted sequentially with different solvents to obtain starch with a low yield of 18.23%, containing less than 1% protein and fat contents. A schematic diagram for the isolation of Great Northern bean starch is presented in Figure 1. Biliaderis et al. (1979, 1981a,b) prepared purified starches by a wet-milling process to study molecular weight distributions of starches from various legume seeds. The seeds were ground with water in a single disc mill to give a coarse slurry. The slurry was defibered by a screen and was centrifuged. Further purification was obtained by passing the

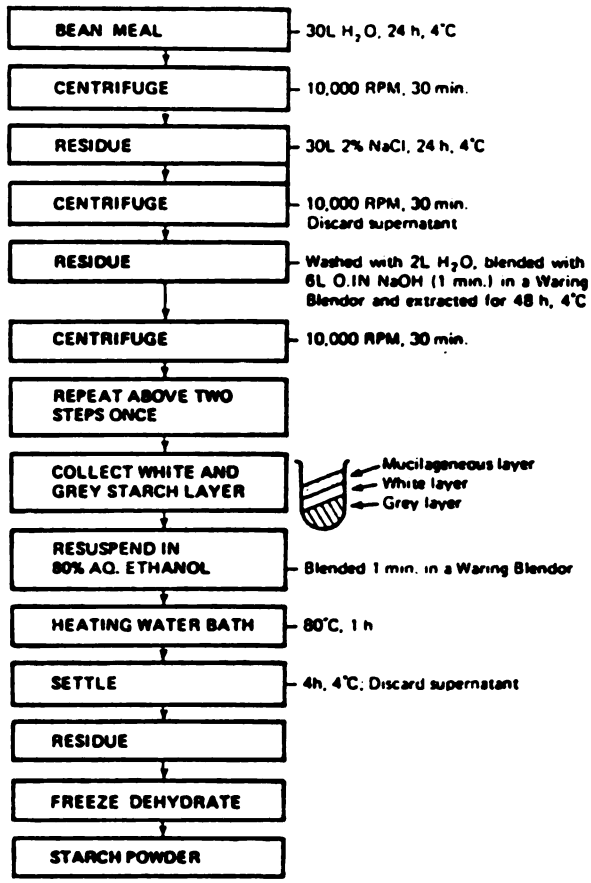


Figure 1. Flow diagram for the isolation of Great Northern bean starch (Source: Sathe and Salunkhe, 1981c)

slurry through a counter-current washing unit and the starches were then dried. Final purification of these starches was done by repeated washing with 95% ethanol and screening (44μm). Purified starches were then dried in a vacuum oven. Proximate analysis data showed these purified legume starches had very high starch content (>94%) with trace amount of protein, lipid, and crude fiber.

The production of protein concentrates from dry edible beans has been reported by several researchers (Plant and Tulsiani, 1969; Satterlee et al., 1975; Luh et al., 1975; Polit and Sgarbieri, 1976). Chang and Satterlee (1979) produced bean protein concentrates containing 72% to 81% protein by extracting bean flours with a dilute salt solution followed by acid precipitation and subsequent centrifugation. Figure 2 shows the isolation procedures to produce the bean protein concentrate. Preparation of protein concentrates from Great Northern bean flour by Sathe et al. (1981b) involved extraction of the flour with 0.5% Na_2CO_3 (w/v) at a flour/solvent ratio of 1/10 and followed by centrifugation, dialysis, and lyophilization. Protein content of the resulting concentrate was as high as 85.4% on dry weight basis.

Isolation procedures suited for commercial production of both protein isolates and refined starch of field peas and horsebeans were developed by Vose (1980). The dehulled seeds were pin-milled and slurried with 0.03 N NaOH at a solid/liquid ratio of 1:4 (w/v). The resultant slurry was screened to remove the fiber fraction and centrifuged to recover the crude starch fraction. Starch was further purified using a series of liquid cyclones incorporating a counter-current wash. Purified starches containing nitrogen of less than 0.07% were produced. A 95% starch yield was obtained from both field peas

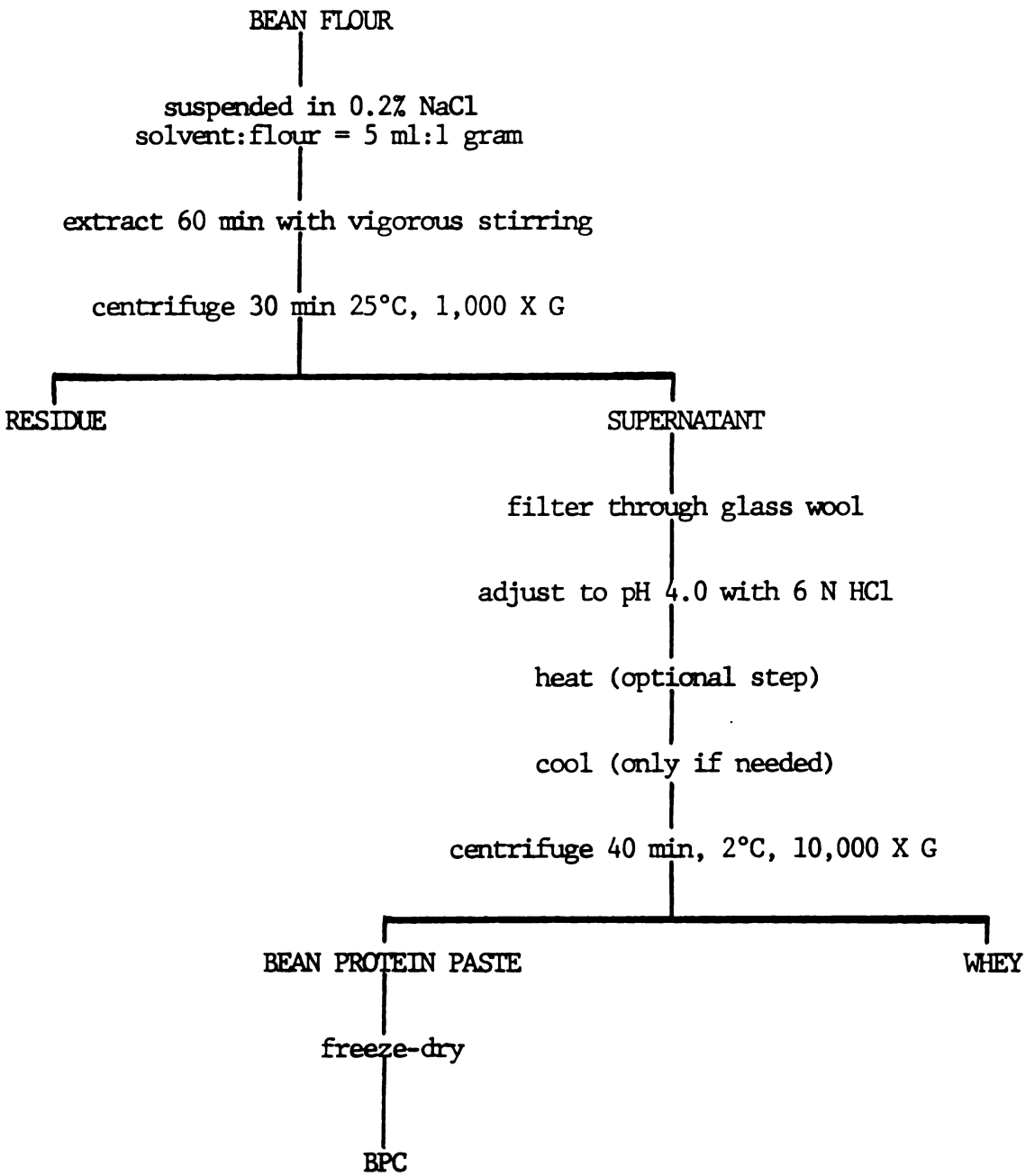


Figure 2. Flow diagram for the isolation of bean protein concentrate (source: Chang and Satterlee, 1979)

and horsebeans. The protein purification process was developed using ultrafiltration techniques and an approximate overall 82% recovery of seed nitrogen was achieved.

Although wet processing resulted in high yields and high percentage values of protein and starch in their concentrates, this method requires significant energy to dry the final products, generates large quantities of effluent which may have high nutritive value, and reduces yields by the loss of wet by-product streams.

Dry Milling and Air-Classification

In recent years, many researchers have developed techniques in milling and fractionation to produce flour products from field peas, horsebeans, faba beans, navy beans, and other legume seeds. Milled products, such as whole flour, hull flour, and air-classified protein and starch fractions from beans, have possessed selected functional properties with good nutrient retention. A number of studies on milling of legume flours and incorporation of flour into food products have been reported.

Raw Beans. Chemical studies of starch and protein fractions were conducted by Vose et al. (1976). Pin-milling of field pea and horsebean seeds, either whole or dehulled, yielded flours that contained two distinct populations of particles. Air-classification techniques were employed to separate these particles into protein and starch concentrates based on both their size and density. The protein fraction contained 60% to 70% protein with adequate lysine and low methionine. The starch fraction contained up to 80% of a 32% to 34% amylose starch. It was demonstrated that the use of air-classification to produce these

concentrates had relatively low capital requirements without the need for costly effluent disposal operations.

In studying the functional characteristics of field pea starch, Vose (1977) applied the same technique to produce a flour containing 78% starch. This flour was then further refined by slurrying, filtering, washing, and drying to yield a white starch containing less than 0.06% nitrogen. He found that starches from both peas and wheat were susceptible to damage by pin milling, whereas the smaller granules of corn starch were less susceptible.

Because pin milling and air-classification of field peas did not completely separate the protein from the starch fraction, Reichert and Youngs (1978) initiated a study to elucidate the sources and chemical characteristics of the residual protein associated with air-classified pea starch. Air-dried peas were dehulled in a plate mill. The dehulled peas were pin-milled and air-classified to obtain crude protein and green starch fractions at protein contents of 54.6% and 8.1%, respectively. Purification of the starch fraction by repeated pin milling and air-classification reduced its protein content and yield. This is due to the removal of the protein bodies which attached to starch granules and agglomerates. Water washing the starch granules suspended chloroplast membrane residues and solubilized most of the remainder of the nitrogen. There were more acidic and fewer basic amino acids in air-classified starch than in the protein concentrate.

Milling of faba beans to produce cotyledon flour was conducted by Watson et al. (1975); however, a low yield of 75.9% was obtained due to the particular physicochemical properties of these beans. D'Appolonia (1977) modified Watson's method by first removing some of the seed coat after the prebreak with a U.S. 710 μ Tyler sieve.

Although there was no chemical analysis data reported, sifting after the prebreak might have improved cotyledon flour purity. This bean flour was used for bread-making studies. Morad and Finney (1980) suggested a laboratory scale milling process, using a Hobart grinder and a repeated sieving and grinding procedure, that gives an 88% extraction cotyledon flour with only 2% to 4% hull. The result of this simple extraction process was compatible to that obtained by hand-peeling methodology.

The production of navy protein concentrate through air-classification was conducted by Patel et al. (1980) to assess the impact of this processing on the amino acid and mineral distribution in the resulting flour fractions. They found that navy bean flour and its fractions had a relatively high lysine content and a low sulfur amino acid content. The protein concentrate with its desirable amino acid and mineral profile was shown to have potential as a supplement in cereal-based products. The starch fraction may be used as a binding agent in extruded non-cereal products or may be used in non-food applications.

Four varieties of white bean or navy bean (*Phaseolus vulgaris* L.) and their air-classified fractions were analyzed for amino acid and proximate composition by Sahasrabudhe et al. (1981). In this study, clean seeds were dried in an air oven to facilitate dehulling. The cotyledons were separated from the hulls by air aspiration and pin milled into flours. The pin milled flour was air-classified into fines (high protein) and coarse fractions in a spiral air-classifier. The coarse fraction was reground and reclassified into high protein and low protein (starch) fractions. The protein enriched fraction (31% to 35% by wt) prepared by air-classification of finely ground dehulled flour

contained 50.3% to 57.5% protein with about 3.5% lipid in all varieties. The starch fraction (53% by wt) contained 7.4% to 8.5% protein with only 0.6% lipid. The stachyose content of the protein fraction was, on the average, four times that of the starch fraction accounting for more than 50% of the total. The lipids and the oligosaccharides were concentrated in the protein enriched fraction. The amino acid profile is characteristic of the legume proteins with a high lysine and low sulfur amino acid content.

Tyler et al. (1981) employed similar procedures as described by Sahasrabudhe et al. (1981) to study the separation efficiency, yield, and composition of the starch and protein fractions from eight grain legumes. After the first air-classification process, the starch fractions contained 58.0% to 76.1% starch and 7.7% to 20.1% protein, whereas the protein fractions contained 49.3% to 75.1% protein and 0.0% to 46% starch. The starch fraction, after the second air-classification process, contained 71.0% to 85.9% starch and 4.0% to 10.4% protein, and a second series of protein concentrates contained 38.0% to 68.2% protein and 0.4% to 16.6% starch. Differences in protein separation efficiency (PSE) among legumes were significant, but differences in starch separation efficiency were not. They concluded that on the basis of PSE and the protein contents of the two protein fractions, mung beans and lentils were the most suitable legumes for air-classification, and lima beans and cowpeas were the least suitable.

Roasted Beans. Legume seeds have relatively high protein content and account for a significant proportion of the protein in the human diet. However, legume seeds contain antinutritional factors which will exert undesirable effects on their nutritive value if they are not inactivated (Puztai, 1967; Jaffe, 1975).

Read and Haas (1938) were among the first to recognize trypsin inhibitor in plant material. Bowman (1944) described trypsin inhibitors in navy beans, soybeans, and corn, and suggested that a heat-labile protein in the aqueous extract of navy beans and soybeans, which inhibited the in vitro digestion of casein by trypsin, might account for the low nutritive value of raw legumes.

Among the many antinutrients present in plant foods are a group of heat-labile proteins known as lectins or hemagglutinins. They are found in many commonly eaten foods (Nachbar and Oppenheim, 1980), but are probably most concentrated in legumes. Lectins are toxic when ingested in large quantities. Diets containing raw bean meal have been shown to be responsible for decreased growth and death in rats (Jaffe, 1980). Cases of toxicity have been reported in humans who had eaten raw or partially cooked red kidney beans (Noah et al., 1980).

Increases in nutritional quality have been demonstrated by heating soybeans to destroy the heat labile trypsin inhibitory compounds. Hemagglutinins can also be partially or wholly eliminated by heating soybeans (Liener and Hill, 1953) and other common beans (Honavar et al., 1962; Bressani and Elias, 1974).

The nutritional composition of dry navy beans is ideal for delivery of protein and minerals if beans are properly prepared and positioned in the diet. Dry beans contain various metabolic inhibitors which must be inactivated or eliminated prior to consumption if maximum nutrient potential is to be derived.

Kakade and Evans (1963) reported that the antitrypsin factors in navy beans could be readily destroyed by autoclaving at 121°C for 5 min. Dry roasting procedures will provide a means to eliminate the undesirable antinutritional factors without high energy and water input. Granular

bed heat exchangers have been used in roasting navy beans (Carvalho et al., 1977). In this study, dry roasting of navy beans in a bed of salt at 190°C for 20 sec or 220°C for 10 sec, resulted in a 70% to 80% reduction in trypsin inhibitor activity.

It was noted that when raw legumes are ground without pretreatment, they develop undesirable odors and flavors which persist after cooking. Lipoxidases have been considered responsible for the presence of off-flavors by catalyzing formation of hydroperoxides from unsaturated fatty acids (Kon et al., 1970). The lipoxidase activity occurs in pulses and oilseeds as well as in soybeans. Smith and Circle (1972) reported that dry heat treatment for 6 to 8 min at 104°C to 105°C completely inactivated this enzyme.

Process condition (i.e., product temperature) had a significant effect on the degree of achieved inactivation (Aguilera et al., 1982a). The effects of three variables (bean temperature, bean/bead ratio, and residence time) at two levels (240°C and 270°C, 1/10 and 1/15, 1 min and 2 min, respectively) were tested in eight runs. They found that trypsin inhibitors were more heat-resistant than were hemagglutinins. The antitryptic activity in raw beans was reduced to 92% by the lightest roasting, and to a minimum of 22% under the harsher conditions. Residual hemagglutinin activities, however, were much lower, varying from 48% to 1% between the extremes of roasting conditions.

In the same study, Aguilera et al. (1982a) reported that water soluble nitrogen decreased as product temperature increased due to protein insolubilization at high temperature. Water holding capacity (WHC) decreased initially with mild roasting and then increased at high roasting temperatures. Severe roasting increased WHC by almost 60%. Gel - forming capacity decreased with increased degree of roasting. Cold

paste viscosities of roasted products were notably higher than those of the raw beans. They also concluded that appreciable changes did not occur in starch granule integrity during roasting.

In another study by Aguilera et al. (1982b), navy beans were also dry roasted in a particle-to-particle heat exchanger before milling. Roasted navy beans were ground to produce whole bean flour (WBF) and hull flours. Dehulled bean flours were then air-classified to obtain high protein (HPF) and high starch (HSF) flours. WBF averaged 1.92% fat and 25.8% protein. HSF and HPF contained 15.6% and 43.1% protein content, respectively. It was reported that greater protein shift may be accomplished by finer grinding and adjustment of the cut point. The activity of antinutritional factors, including trypsin inhibitor and hemagglutinins, was reduced in HPF by the roasting treatment.

Physicochemical Properties of Bean Flours

Composition of Dry Beans

Dry beans contain about 6% to 10% moisture, 25% to 30% proteins, and up to 60% carbohydrates. These carbohydrates include starch, mono- and oligosaccharides, and other polysaccharides. Starch constitutes the major portion of legume carbohydrates (Sathe and Salunkhe, 1981a,b,d; Cerning-Beroard and Filiatre, 1976; Naivikul and D'Appolonia, 1978). Total sugars, including mono- and oligosaccharides, represent only a small percentage of total carbohydrates in dry bean seeds. Oligosaccharides of the raffinose family predominate in most legume flours and account for a significant part (31% to 76%) of the total sugars (Naivikul and D'Appolonia, 1978; Sathe and Salunkhe, 1981c; Akpapunam

and Markakis, 1979). Legumes also contain appreciable amounts of fiber components (1.2% to 13.5% which consists of cellulose, hemicellulose, pectin, and cutin substances (Labaneiah and Luh, 1981). Uebersax et al. (1983) reported that dietary fiber values in dry-roasted whole flours were 7.88% for navy beans, 6.47% for pinto beans, and 4.92% for black beans. Hemicellulose was the major fiber component in these flours.

Other components in legumes include fat and ash. As reported by Naivikul and D'Appolonia (1978) from five legumes tested, fat content ranged from 2.58% (mung bean) to 4.93% (navy bean), and ash content ranged from 2.25% (faba bean) to 4.30% (mung bean). Dry-roasted navy beans contained about 2% fat and 5% ash as reported by Uebersax et al. (1980).

Since starch and protein are the major constituents in legumes, their concentrates, either produced from wet extraction or air-classification, have been studied extensively for their chemical, physical, and functional properties.

Starch Flours

Two types of polysaccharide molecules are present in starch. Both are homoglycans of D-glucose, namely, amylose and amylopectin. The amylose fraction of starch is essentially linear chains of 500 to 2000 D-glucose units interlinked by α-1,4 glycosidic bonds whereas amylopectin is branched molecules with α-1,4 and α-1,6 glycosidic likages with about 5,000 to 20,000 units. Biliaderis et al. (1979) studied the molecular weight distribution profile for several legume starches. They reported that the major portion of legume starches has molecular weights higher than 2×10^6 and over 90% of the starch has a molecular weight above 4×10^4.

Native cereal starches consist of about 30% amylose and 70% amylopectin. Some waxy cereal starches contain only amylopectin. High amylose starch, as bred in maize, may have as much as 80% amylose. In legumes, amylose generally constitutes a significant portion of the starch, ranging from 10% to 60% (Reddy et al., 1984). The amount of amylose in the starch influences starch solubility, lipid binding, and other functional properties. Amylopectin is also believed to be associated with the solubility of starch granules.

In the cell of plants these starch molecules are organized into microscopic packages or granules. Starch granules of beans from different plants have characteristic size and shape and their diameters may vary from 1 μm to 80 μm. Most bean starch granules are slender, although spherical, ovoid, elliptical, and irregular shapes are also found. This variation in granule size and shape may be due to genetic control and seed maturity. The granules remain essentially intact during modification or processing techniques, such as milling, used for preparation of starch as a food ingredient.

Plants normally elaborate and arrange starch in the form of microscopically small grains in which a mixture of linear and branched molecules of starch lie with their long axes radially in concentric rings and perpendicularly to the grain surface at which they are laid down (French, 1972; Sterling, 1978). Compact and highly ordered crystalline states are present in certain parts of each ring. As estimated by Rundle et al. (1944a,b), the crystalline region of most native starches comprise 50% to 60% of the total starch. These crystalline regions or micelles are held together by hydrogen-bonding. The amorphous regions which are more loosely packed and easily accessible to water exist between the micelles within each concentric

ring and between concentric rings. Orientation of molecules to parallel one another causes the starch granules to polarize light and thus to become birefringent.

Chemical composition of several legume starches has been determined (Schoch and Maywald, 1968; Naivikul and D'Appolonia, 1979; Sosulski and Youngs, 1979; Vose et al., 1976). Faba bean starches isolated by wet-processing and by air-classification were studied for their properties by Lineback and Ke (1975) and Lorenz (1979), respectively. Sosulski and Youngs (1979) and Lai and Varriano-Marston (1979) reported that the Brabender viscosity pattern of the starches appeared to be determined by the extent of swelling of the starch granules and the resistance of the swollen granules to dissolution by heat or fragmentation by shear. It was found that leaching of soluble starch from the granules upon heating may have contributed to the viscosity pattern (Allen et al., 1977; Lai and Varriano-Marston, 1979).

Schoch and Maywald (1968) isolated starches from seven legumes and studied their properties. Starches from lentil, yellow pea, navy bean, and garbanzo showed restricted swelling patterns similar to those of cross-bonded starches. These properties were attributed to a relatively high content (30% to 40%) of linear fractions in these starches. Lima bean starch, with high linear content, showed higher swelling during pasting and the viscosity was similar to that of corn starch. Wrinkled-pea starch which contained 75% linear fraction behaved similarly to high amylose corn starch.

Starches of field peas and horsebeans were isolated by Vose (1980) to study their functionality. He reported that these legume starches contained 32% to 35% amylose and had restricted swelling characteristics typical of type C starches. Gels were rigid, opaque, and friable with

a firmer texture than that of comparable corn gels. However, it was found that gel shrinkage occurred following storage at 5°C, resulting in 13% to 15% syneresis losses.

Naivikul and D'Appolonia (1979) compared legume starches with wheat starch. The amylogram curves of the legume starches showed higher initial pasting temperature and higher viscosity than did wheat starch, which indicated a higher resistance to swelling and rupture. Water-binding capacity of legume starches was generally higher than that of wheat starch.

Great Northern bean (*Phaseolus vulgaris* L.) starch was wet-extracted and studied for its functional properties by Sathe and Salunkhe (1981c). They reported that amylose content of the starch was 10.2% (starch basis). The starch had good water and oil absorption capacities at room temperature and formed a stable gel at concentrations of 7% and above (w/v). This bean starch also showed a restricted swelling pattern on the viscoamylogram. The same starch was used by Sathe et al. (1981a) to investigate its solubility and swelling. They found that both properties were temperature and pH dependent. Solubility of the starch was highest at pH 6.0. Both acetylation and oxidation resulted in reduced swelling of starch over a pH range of 2 to 10. Addition of fatty acids to the starch reduced the Brabender viscosity and raised the gelatinization temperature.

Chemical composition and functional characteristics of white bean starch produced by air-classification technique were also studied (Sahasrabudhe et al., 1981). The starch fraction (53% by wt) contained an average of 30% amylose and gave a torque-temperature curve typical of legume starches with slow swelling, no breakdown at constant temperature and shear, and a high set-back.

Protein Flours

Dry legumes constitute an important source of dietary protein for a major portion of the world's population and beans have been the major legume used for human consumption.

Cereals are deficient in lysine, whereas dry beans are rich lysine sources. Although production of lysine-rich flours from legumes may fortify the traditional cereal-based foods, the high carbohydrate and low protein content of these flours may cause adverse effect when incorporating into food products (Patel et al., 1977). Protein concentrates or isolates from horsebeans and lima beans with superior functional properties have both found wider food application than have flours (Patel and Johnson, 1975; Maneepun et al., 1974).

Dry bean proteins are complex in nature with the majority of the proteins being globulins and albumins. Sathe and Salunkhe (1981b) reported that protein content of the Great Northern beans was 26.1%. Albumins and globulins accounted for 21.18% and 73.4% of the total proteins, respectively. Na_2CO_3, K_2SO_4, sodium dodecyl sulfate, and NaOH at respective concentrations of 0.5%, 5%, 5% (all w/v), and 0.02N were found to be better protein solubilizers among several solubilizing agents tested, with the solubilized protein being 207.5 mg per gram bean flour. The electrophoretic characterization of the bean flour, albumins, globulins, protein concentrates, and protein isolates, produced through wet-extraction, was also conducted in this study.

Functional properties of these proteins were further studied by the same workers in another study (Sathe and Salunkhe, 1981a). They reported that protein concentrate had the highest water and oil absorption capacity of 5.93 g/g and 4.12 g/g, respectively. Protein

concentrate showed the highest emulsion capacity, while albumins showed the highest emulsion stability. This investigation also indicated that the albumins were better emulsifiers than globulins in relation to both capacity and stability. Foaming ability of the flour protein studied was inferior to that of egg albumin powder.

The protein enriched fraction (31% to 35% by wt) prepared by air-classification of ground cotyledons contained 50.3% to 57.5% protein as reported by Sahasrabudhe et al. (1981). Water hydration capacity and heat thickening property of the protein fraction were found to be similar to other vegetable proteins indicating a potential use in processed foods.

Storage Stability of Bean Flours

In response to the increasing need for dry products in convenience form, Morris (1961) developed cooked dry bean, pea, and lentil powders for use in a variety of dry mixes, such as soup and dip for crackers. With the growing consumer interest in this convenience food area and the declined dry bean consumption per capita in the United States, research has emphasized the production of acceptable convenience forms of dry beans (Rockland, 1966; Hoff and Nelson, 1966; Bakker-Arkema et al., 1967, 1968). The instant legume powders produced from both drum dehydration and spray drying (Bakker-Arkema et al., 1967) were reported to possess good flavor, color, and reconstitution characteristics, although powders from the drum drier were preferred.

Quality Changes during Storage

Quality changes, including protein solubility, lipid oxidation, and browning, of these dry bean powders or flours during storage have been a major concern.

Protein Solubility. Melnick and Oser (1949) indicated that storage of foods over extended periods of time appears to cause impairment of the nutritive value of the protein. These changes were similar to those caused by excessive heat processing. Most of these changes did not result from amino acid destruction, but rather from the formation of resistant peptide linkages which slow down the rate of enzymatic digestion, thereby disrupting the release of amino acids for absorption. Henry and Kon (1948) stated that the value of protein is determined not only by the concentration and digestibility of the protein, but by the availability of its amino acids and its essential amino acid pattern.

Henry and Kon (1950) argued that it was possible to alter the nutritive value of protein without the destruction of amino acids. They explained that linkages between reducing sugars and cross-linkages between proteins or peptide chains were formed which contributed to resistance to proteolytic action. Altered enzyme action produced an array of unabsorbed atypical peptides.

Products from Maillard reaction have been found as being the cause of decreased protein nutritive value in foods. In the study of the deterioration of dried skim milk during storage, Henry and Kon (1948) indicated that the loss in the biological value of milk proteins was through the formation of enzymatically resistant Maillard reaction products. Melnick and Oser (1949) also concluded that it was the slowed rate of enzymatic hydrolysis which contributed to lowered

biological value in stored, browned foods. The amount of lysine released in browned foods was one-fourth that released from unbrowned products. McInroy et al. (1945) also reported that the formation of browning products including enzyme and acid resistant linkages contributed to decreased protein value.

Oxidation of food lipids has been reported to be associated with the loss of nutritive value of proteins. Buchanan (1969a,b) found that lipid oxidation of products resulted in decreased digestibility of leaf protein concentrate due to the formation of complexes with proteins. Three types of deteriorative processes were reported by Jones and Gersdorff (1941) in stored wheat flour: decreased protein solubility, partial breakdown of proteins, and decreased soluble nitrogen digestibility. Lipid oxidation was found to be one of the factors to cause the reduced digestibility.

Non-Enzymatic Browning. Non-enzymatic browning is characterized as a sequence of reactions without enzymatic catalysis which produces desirable or undesirable changes in food systems. The carbonyls involved in these reactions are derived either from water soluble reducing sugars or from lipid oxidation. A complete and thorough review of the browning reactions was made by Hodge and Osman (1976).

Among these reactions, Maillard reactions are often encountered in foods and are referred to as a complex group of reactions between the carbonyls or reducing sugars and free amino groups leading to production of brown pigments and aromatic compounds. Miller (1956) indicated that protein quality of foods is slightly reduced during drying, due to browning reactions. Patton et al. (1948a,b) also showed in model systems that heating casein at 96.5°C for 24 hours caused loss of amino acids by Maillard browning reaction. Friedman and Kline (1950)

stated that the presence of a reducing sugar and a protein held under mild conditions would cause reduction in the biological value of protein. Histidine, threonine, tryptophan, phenylalanine, lysine, and methionine were rendered unavailable by the browning reactions.

The carbonyl reactants derived from lipid oxidation may also react with proteins leading to non-enzymatic browning. Jones and Gersdorff (1941) and Tappel (1955) found that these carbonyls arising from oxidized lipids were able to interact with proteins to form browning products. Amino acids in proteins reacted with carbonyls and became unavailable. Koch (1962) also reported the involvement of oxidized lipids in browning reactions in freeze dried foods. Dugan and Rao (1972) further described the role of aldehydes from lipid oxidation in the browning of stored dried foods.

Lipid Oxidation. Fats present in foods may become rancid as a consequence of oxidation. This oxidative rancidity accompanied with undesirable flavors is a major cause of food deterioration. Lea and Parr (1961) reported that flavor defects arose from the oxidation of lipids. The polyunsaturated fatty acids in glycolipids and phospholipids developed painty, grassy, and fishy odors and flavors. In the oxidation process it is assumed that hydroperoxide groups attach to the carbon atom of unsaturated fatty compounds, and subsequently the breakdown of hydroperoxides gives a chain reaction of autoxidation termed a free radical chain mechanism. This chain sequence can be described by three stages as follows:

Initiation $\quad RH \rightarrow R\cdot$

Propagation

$$R\cdot + O_2 \rightarrow ROO\cdot$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot$$

Termination

$$ROO\cdot + ROO\cdot \rightarrow ROOR + O_2$$

$$R\cdot + R\cdot \rightarrow RR$$

$$ROO\cdot + R\cdot \rightarrow ROOR$$

Roubal and Tappel (1969) studied the transient free radicals in a peroxidizing lipid-protein model system. They reported that protein damage was due to the destruction of amino acids and the free radicals were found to be a major cause of this destruction.

The stability of an oxidizing polyunsaturated system was related to the hydroperoxide (ROOH) content (Privett and Blank, 1962). The lower the ROOH level found in the system, the longer the stability could be obtained. The destruction of the amino acid cystine through ROOH oxidation in autoxidizing lipids in a model system was examined by Rice and Beuk (1953) and Lewis and Wills (1962).

In studing the lipid-protein system, Fletcher and Tappel (1971) indicated that the peroxidizing polyunsaturated lipid reacted with amino acids to give fluorescent compounds. They theorized that this process involved the reaction of carbonyls (secondary products of lipid oxidation) with primary amines to produce the Schiff base imine products. In contrast to their conclusion, Roubal (1971) believed that the process, which resulted in the greatest amount of amino acid loss in an oxidizing lipid-protein system, came from the free radical attack on the proteins. This was later explained by Gamage and Matsushita (1973) and Matsushita (1975): both radical and non-radical products of peroxidized lipids can polymerize proteins.

A variety of techniques can be employed to detect the extent of lipid oxidation. Direct methods of analysis to follow changes in reactants include the measurement of oxygen uptake (Karel and Labuza, 1968) and free radical formation (Roubal, 1971). Measurement of end products, such as fluorescence (Matsushita, 1975) and thiobarbituric acid reactive substances (Bidlack and Tappel, 1973), is also frequently used. Measurement of the change in unsaturated fatty acid content, determined by gas-liquid chromatography (Buttery et al., 1961a,b), has been used to indirectly detect lipid oxidation. Changes in the content of extractable lipid fractions (Lea and Parr, 1961) is another indirect method.

Factors Affecting Flour Stability

Stability studies with cooked lima bean powders were conducted by Burr et al. (1969) using sensory methods to evaluate flavor change. The product was stored at three temperatures (-23°C, 22°C, and 38°C), either air- or nitrogen-packed, with the initial moisture contents of 4%, 5%, and 10% for various periods of time. The most favorable conditions for storage were powder with 4% moisture content, nitrogen-packing, 3 ppm BHT, and 22°C temperature. Flavor changes in this sample were not detected until after eleven months of storage. All air-packs tested were rather unstable. Stored at 22°C, they showed flavor changes after about 2 months, and at 38°C, after 1 month. Shelf-life of powders were extended by nitrogen-packing at all moisture levels and temperatures. This study also indicated that powder with 4% moisture was slightly more stable in all instances than were the 5% moisture samples. Powders with 5% moisture were consistently evaluated to be fresher than those with 10% moisture content.

Counter (1969) studied the storage stability of atmospheric and pressure cooked drum dried navy bean powders. Products were sealed in cans and stored at 0°C, 20°C, and 40°C for up to 120 days. He reported that the maximum shelf life for this powder was between 90 and 120 days without the use of shelf stabilizers. Storage at 0°C increased the shelf life about 30 days over those stored at 40°C. The major changes observed in this study were the oxygen content in the headspace and the lipid and protein fractions. Results indicated that oxygen content decreased significantly with increased storage temperature and time. The free fatty acid content increased and nitrogen solubility decreased with storage time; however, no significant changes were found in the total reducing sugar content or in color.

Flours made from cereals or legumes are not processed to greatly reduce their natural microflora. As a result, these products are likely to contain molds, yeasts, and bacteria which will grow under desirable moisture levels. Frazier and Westhoff (1978) indicated that mold growth occurs even under low moisture levels, whereas yeasts and bacteria will grow under higher moisture conditions. A study was conducted by Bothast et al. (1981) to evaluate the effects of moisture and temperature on the microbial growth of wheat flour and corn meal during storage. Samples were stored at moistures ranging from 11% to 18% and temperatures of 25°C and 34°C for 18 months. It was reported that, in general, bacteria did not grow under the relatively dry conditions used in this study and their numbers decreased with time. Mold counts increased in products stored at 15% and 18% moisture, reaching maximum numbers by three to six months, and then decreased during the remaining storage period. They concluded that product quality cannot be maintained beyond six months at 15% moisture and 25°C or beyond 15 days at 18% and 25°C. Quality

deteriorates more rapidly at 34°C than at 25°C at these moisture levels. Perera et al. (1979) studied vitamin B_6 stability in enriched white flour and reported that this vitamin was stable when stored at room temperature or in a cold room for six months.

The storage stability studies mentioned above have shown quality changes of products as affected by storage conditions such as temperature, time, initial moisture content, atmosphere, and presence of antioxidant. In addition to these factors, equilibrium relative humidity (ERH) or water activity (a_w) of the product should also be considered. It has been generally recognized that ERH values or a_w are more closely related to food product stability than to moisture content of foods. The definition of a_w and its relationship to the stability of foods was reviewed by Labuza (1968), Rockland (1969), and Labuza et al. (1970). Food products stored in various relative humidities will take on or give up water and reach equilibrium moisture content (EMC). The EMC is then plotted against the ERH or a_w surrounding the product to obtain the sorption isotherm. The hydration process of the food material can be explained on the sorption isotherm curve with three ranges of a_w: monolayer water region (<0.3), multilayer region (0.3 to 0.7), and capillary condensation region (>0.7) (Wolf et al., 1972).

Water content, when expressed as water activity, has a decisive effect on the stability of low moisture foods. Labuza et al. (1970) discussed the dependence of various deteriorative reactions on a_w. Lipid oxidation is found most rapid at low a_w and its rate decreases as a_w is increased. The rate increases again at even higher a_w. Non-enzymatic browning increases with increased a_w reaching a maximum and then decreases due to the dilution of the reactants. These two reactions are the major deteriorative processes often encountered in low- and

intermediate-moisture foods. Growth of microorganisms at high a_w's is another process that limits food stability.

The theoretical aspects of the reactions between a_w and deteriorative process of certain food components in model systems have been carried out and summarized by Labuza et al. (1970); however, very few studies have discussed the change of quality characteristics of low moisture foods in relationship to a_w. Burr et al. (1969) studied the stability of lima bean powder with selected initial moisture content; however, only flavor was employed as a quality index. In the storage study of navy bean powder, Counter (1969) stored two products at two constant moisture levels and did not report quality change of powders as a function of a_w. Wolf et al. (1972) concluded that storage conditions which produced marked changes in the quality of dehydrated apple, pork, and rice were associated with the changes of sorption hysteresis.

The significance of a_w to the deterioration rate of the quality and nutritive value of stored food products was evaluated by Henry and Kon (1948) and Lea and White (1948) for dry skim milk. Samples were equilibrated under various relative humidity levels to obtain certain moisture contents. Henry and Kon (1948) demonstrated that high moisture of 7.6% caused a significant decrease in protein quality during 37°C storage within two months. Samples stored at 3% moisture and 37°C showed little chemical deterioration. Lea and White (1948) found that the powder with 7.6% moisture at 37°C discolored most rapidly and showed the greatest insolubility. They reasoned that the cause of this deterioration was the reaction of ε-NH_2 groups of the amino acid lysine, with the reducing sugar lactose, present in the product; this process, therefore, decreased powder solubility and protein quality.

They concluded that a_w in the powder determined the rate of deterioration.

Guadagni et al. (1975) conducted a study to determine stability of commercially prepared pinto bean powder stored in air and under a nitrogen atmosphere at 50°F, 70°F, and 90°F. They found that the development of off-flavor increased with increased storage time up to 100 weeks in both air and N_2 packs. Nitrogen packing resulted in some delay of the off-flavor development. An exponential relation was found between powder stability and temperature in the 50°F to 90°F range.

Love (1975) investigated the effect of storage atmosphere and a_w on lipid and protein content of navy bean powder under accelerated storage conditions at 37°C. It was found that at a_w of 0.11, more lipid oxidation occurred in the neutral lipids and phospholipids of air-stored samples than in those stored in nitrogen. Phospholipids were slightly protected when the product was stored at a higher a_w of 0.23, while the neutral lipids were not protected from autoxidation. Samples stored at 0.23 a_w browned to a greater extent than those stored at 0.11 a_w. This data also showed that the samples which had undergone the greatest amount of non-enzymatic browning also had altered in vitro protein digestibility. Optimum storage conditions were obtained at 4% to 5% moisture content, packing in inert gas with antioxidant, and stored at temperatures not greater than 20°C.

The storage stability of pea flour, pea protein concentrate, and pea starch was evaluated during a one year period at four moisture levels ranging from 3.8% to 13.6% and temperatures of 7°C, 21°C, and 30°C (Sumner et al., 1979). Total bacteria, coliform, yeasts, molds, and psychrotrophs were found to increase initially and were followed

by a steady decline. They reported that the stability of the pea products was dependent on the ERH which affected microbial growth and enzyme activity, thereby causing deterioration of odor, flavor, and color. An ERH of 60% should provide satisfactory product stability under many conditions; however, at this level the effect of temperature cycling and packaging materials should be considered.

Rheological Properties of Starch Pastes

Colloidal Nature of Starch Pastes

The air-classified high starch flour constitutes more than 50% of the total yield. Its major component is starch. The principle uses of starches are as colloids, pastes, and gels. Starch, as a thickening agent, helps to achieve a desired consistency in food products such as gravies, sauces, pie fillings, and puddings. Starches are also used as diluents in chemical and pharmaceutical industries, as carriers in cosmetics and tablets, and as binders in paper industry.

A thorough knowledge of the physicochemical changes of starch granules during heating and cooling is essential for proper understanding of the rheological properties and viscosity changes of starch suspensions and starch pastes.

Gelatinization. The strength of micellar network of linear and branched molecules present in the starch granules controls the behavior of the granules in water (Leach, 1965). Starch granules have limited water sorption capacity and ability to swell reversibly due to the limited elasticity of their micellar network system. Cold water can penetrate amorphous regions of the granule without disturbing the

micelles and swelling cannot be detected unless under microscopic examination. When the hydrogen bonds in the starch suspensions are disrupted by sufficient heat, the hydration of the network is encouraged and an irreversible process of swelling is initiated. The temperature at which this process starts is called the gelatinization temperature or gelatinization range. At this temperature, some of the granules swell tangentially and lose their birefringence. With the initial rapid swelling of starch granules, the clarity of the suspension suddenly increases. Further heating causes more loosening of the network, allowing even more water to enter to enlarge the granule. The swollen granules, however, are still held by the micellar network to remain whole unless sufficient heat or agitation is applied to tear then apart.

It was pointed out that the larger the starch granules present in the system, the lower the gelatinization temperature. The extent of swelling of starch is a function of temperature and genetic constitution. Branched molecules are considered particularly related to the swelling of starch (Waldt and Kehoe, 1959).

Attaining the gelatinization range with subsequent swelling of the granules is accompanied by the increase in viscosity. The viscosity is caused not only by the properties of the individual swollen granules coming into contact with each other but by the molecules released from the granules (Miller et al., 1973). The molecules, mainly amylose, which are dispersible in hot water, leach from the swollen granules and into the surrounding aqueous phase. When this swelling process reaches the point where the granules occupy the entire volume, the solubles in the exudate will rediffuse back into the swollen granules.

As the temperature of the suspension is raised above the gelatinization range, the granules continue to swell if sufficient water is present and become many times their original size. At this stage the granules are very susceptible to thermal or mechanical breakdown due to their highly swollen condition and increasing weakening or bonding forces within the micellar lattice. Prolonged heating of the paste, particularly in the presence of shearing, results in the disintegration of the granules, leading to a colloidal system containing swollen granules, granule fragments, and dispersed starch molecules. Consequently, the viscosity of the paste is reduced.

Retrogradation. When the temperature of the paste is cooled, the amylose molecules which have leached from the gelatinization grains rebond to one another and to branches of amylopectin on the outer edge of granules. Thus they unite swollen starch grains in a network with an increase in viscosity. This recrystallization of gelatinized starch is known as retrogradation. Retrogradation is also regarded as a process in the firming of a starch gel. As time goes on, the gel will shrink and express some entrapped water. This is known as syneresis. Retrogradation of amylopectin can be reversed by heating. However, retrograded amylose cannot be recovered by ordinary heating.

Factors Affecting Paste Viscosity. Rheological data of the interactions of starch with other food ingredients in heating and cooling should be of benefit in formulation of food products containing starch as a thickening agent. Some of the factors affecting the viscosity of starch pastes in foods include sugars, acids, salts, fats and surfactants, starch concentration, heating, and the methods with which starches are evaluated.

In the study of the effect of sucrose on starch properties, Hester et al. (1956) found that sugar decreased the thickness of cooked products when it was added to puddings and soft pie fillings. It decreased the stiffness of the cooled product even more. Because of its hydrophilic character, sugar competes with starch for water, thereby retarding swelling of starch granules. Higher sugar concentration lowers the rate of swelling and thus a lower final viscosity is obtained. Viscosity increase at lower sugar concentration is due to the fact that this small amount of sugar delays the fragmentation of the most rapidly swollen granules without preventing swelling of other granules.

Acid, in the form of vinegar or lemon juice, is often used in starch-thickened foods. Acid reduced the thickness of hot starch paste and the firmness of cool pastes (Hansuld and Briant, 1954). In the presence of heat, acid catalyzes the hydrolysis of starch molecules to dextrins. This fragmentation of swollen starch granules which results from the hydrolysis reduces the thickening power of the starch. Paton (1981) studied the behavior of oat starch in solutions and found that high solution torque developed by cooling the hot paste to 75°C to 80°C was abolished in the presence of acetic acid at pH 3.0.

Effect of a lyotropic ion series on the pasting characteristics of wheat flours was evaluated on amylograms by Medcalf and Gilles (1966). A progressive increase in pasting and peak temperatures of starch was noted from SCN^-, which is among the most potent solubilizing ions, to SO_4^{-2}, which is among the most potent insolubilizing ions. In a study on the effect of sodium chloride on the pasting of wheat starch granules, Ganz (1965) found that the peak viscosity was markedly increased in a Brabender viscoamylograph when a wheat starch suspension was heated in

2.5% NaCl solution. Paton (1981) reported that starch in 0.1N salt solution reduced the torque values of cool paste measured by amylograph and Ottawa Starch Viscometer.

Osman and Dix (1960) found that the temperature at maximum viscosity of 6% corn starch paste decreased progressively from 92°C to 82°C when an increased amount of fat was added from 9% to 12%. These fats, composed mainly of triglycerides with aliphatic chains of 16 to 18 carbons, however, did not affect the maximum viscosity in a Brabender amylograph. The same workers found that addition of surface active agents to the system resulted in large increases in the temperature at which granules noticeably enlarged and in the temperature at which the maximum viscosity occurred. This result was in agreement with that reported by Sathe et al. (1981a) who stated that addition of fatty acids (palmitic, stearic, and linoleic) to purified bean starch reduced the Brabender amylograph viscosity and raised the gelatinization temperature of starch. The effect of lipid components on the viscosity of wheat starch paste was studied by Niihara and Matsumoto (1981). They suggested that the presence of small amount of free fatty acids and monoglycerides may reduce starch paste gelation.

The effect of concentration (2% to 8%) on the viscosity of cassava starch paste during cooking-cooling was conducted by Odigboh and Mohsenin (1974) using the Stormer Viscometer. They reported that the rise to peak viscosity was relatively gradual at the lower concentrations but quite abrupt at the higher concentrations. The temperature of the peak viscosity decreased with the increased concentration studied. Viscosity dropped more rapidly beyond peaks for higher concentration pastes than for lower ones. A similar study by Odigboh and Mohsenin (1975) also reported that the temperature of peak viscosity decreased

with increasing concentration. Bagley and Christianson (1982) stated that viscosity increased very rapidly with concentration above 16% for starch suspensions cooled at 60°C. However, the rapid viscosity increase occurred at lower concentration when cooking temperature was raised to 65°C, 70°C, and 75°C.

The effect of heating on the rheological behavior of starch-water systems is associated with the heating temperature and duration of heating as well as the method with which they are evaluated. A number of workers have studied the starch pastes of various sources for their rheological behavior in relation to the heating and cooling process. This is to be discussed in the following section.

Rheological Property Studies in Food Systems

There are a number of reasons for the food industry being interested in the rheological measurements of fluid products.

Quality Control. Data from these measurements are frequently needed for quality control of the raw materials, ingredients, and final processed products. Such data may also provide information about relationships between product structure and its rheological characteristics. The flow behavior of fluid foods can also be correlated to their sensory properties.

The consistency of a fluid material, for instance, usually expressed in terms of viscosity, is the property which governs its flow behavior and is a measure of internal resistance to flow. The starch pastes have the binding and adhesive properties closely related to their viscosity, and as a result, the viscosity of the paste is usually used to characterize a starch.

In the food industry, viscosity values are used as indices of the consistency of processed starch-containing foods. Parameters, such as time coefficient and shear coefficient, related to breakdown of the starch materials, are used in predicting consistency loss due to agitation of mixing of food ingredients (Muller, 1973). Viscosity data are also useful in evaluating gelatinized starch paste quality in order to assess the suitability of the starch for use in food systems (Albrecht et al., 1960).

Engineering Applications. The rheological data can also be applied to the engineering design of continuous processes in the food industry (Holdsworth, 1971). In the transport of fluid foods, it is necessary to predict flow rate in pipes of various diameters or to determine required pump sizes to achieve specified flow conditions. Rate of heat transfer in relationship to the viscosity of food materials is also important in a process such as dehydration or pasteurization. The prediction of power requirements in agitation or mixing systems is essential in mixing fluid foods. The relationship between the viscosity and power for mixing can be obtained from the empirical charts of Re: $(ND^2\rho/\eta)$ against $(Pg_c/N^3D^5\rho)/(N^2D/g)^Q$ (McCabe and Smith, 1967; Charm, 1963a).

Methods for Rheological Measurements

Two main approaches as described by Sherman (1970) have been used to study the flow properties of dispersed systems. One approach is to explain the relationship between flow characteristics and product microstructure based on a structural rheological model. The other approach is to select a mathematical expression that best relates the data between shear stress and shear rate without considering the structure or

composition of the system. The latter approach permits the researchers to characterize the fluid flow by determining the shear stress over a range of shear rates to draw a flow curve. Starch-in-water systems, being recognized as dispersions, have been studied for their rheological properties using this approach (Kempf and Kalender, 1972; Odigboh and Mohsenin, 1974, 1975; Evans and Haisman, 1979; Niihara and Matsumoto, 1981; Bagley and Christianson, 1982).

A variety of instruments has been used to measure the rheological properties of starch pastes in laboratories or industries. Some of these instruments are designed to simulate the processing or the end use of the starch materials. The data obtained do not provide absolute units. These empirical test procedures indicate whether the samples subjected in practice will differ in their response to the test conditions. Smith (1964) presented a thorough description of many traditional instruments including the Brabender Viscoamylograph, the Corn Industries Viscometer, the Brookfield Viscometer and the Scott Viscometer.

The Viscoamylograph has been used extensively in recent years in evaluating the pasting properties of bean starches (Sathe and Salunkhe, 1981a,b; Morad et al., 1980; Sathe et al., 1981a). It was originally designed to evaluate the baking quality of rye flours that were used to produce breads. This instrument was then applied to study the gelatinization property of wheat and other cereal flours by U.S. cereal chemists in the 1940's (Anker and Geddes, 1944; Brown and Harrel, 1944). The Brabender Viscoamylograph, combining the original Viscograph and the Amylograph into one instrument, has become the most commonly used instrument in laboratories to record the change of viscosity which occurs during the pasting, cooking, and cooling of aqueous starch systems. It is a viscometer consisting of a rotating cup and bobbins for

determining and recording the apparent viscosity through torque measurement at fixed temperatures or temperatures varied at a uniform rate. For viscosity curve, the starch dispersion is heated from 50°C to 95°C at a rate of 1.5°C/min, held at 95°C for certain time, and then cooled down to 50°C at the same rate.

As suggested by Mazurs et al. (1957), the starch pasting properties can be characterized from Brabender data by the five significant points from the curve of the starch used (Figure 3):

A. Peak viscosity --- maximum viscosity reached during heating, regardless of the temperature. Comparison of this point to the point where temperature starts rising gives the gelatinization range.

B. Viscosity when paste reaches 95°C --- the relation of this value to the peak viscosity indicates the ease of cooking the starch.

C. Viscosity after cooking 30 min or longer at 95°C --- this indicates the stability or breakdown of the paste during cooking.

D. Viscosity after cooling paste to 50°C --- a measure of the set-back or retrogradation tendency caused by cooling.

E. Viscosity after 30 min or longer at 50°C --- the stability of cooked paste as it might be used.

The stability of a hot paste is indicated as the difference of the viscosity between point A and point C. Starches with higher swelling power which result in high peaks are more susceptible to breakdown upon cooking and hence exhibit significant viscosity decreases beyond peaks. Higher starch concentrations cause more abrupt increases of the peak, lower pasting temperatures, and more rapid decreases in viscosity (Mazurs et al., 1957). Some starches, such as cross-bonded waxy starch, do not show a peak through this stage. Cross-bonding reduces the

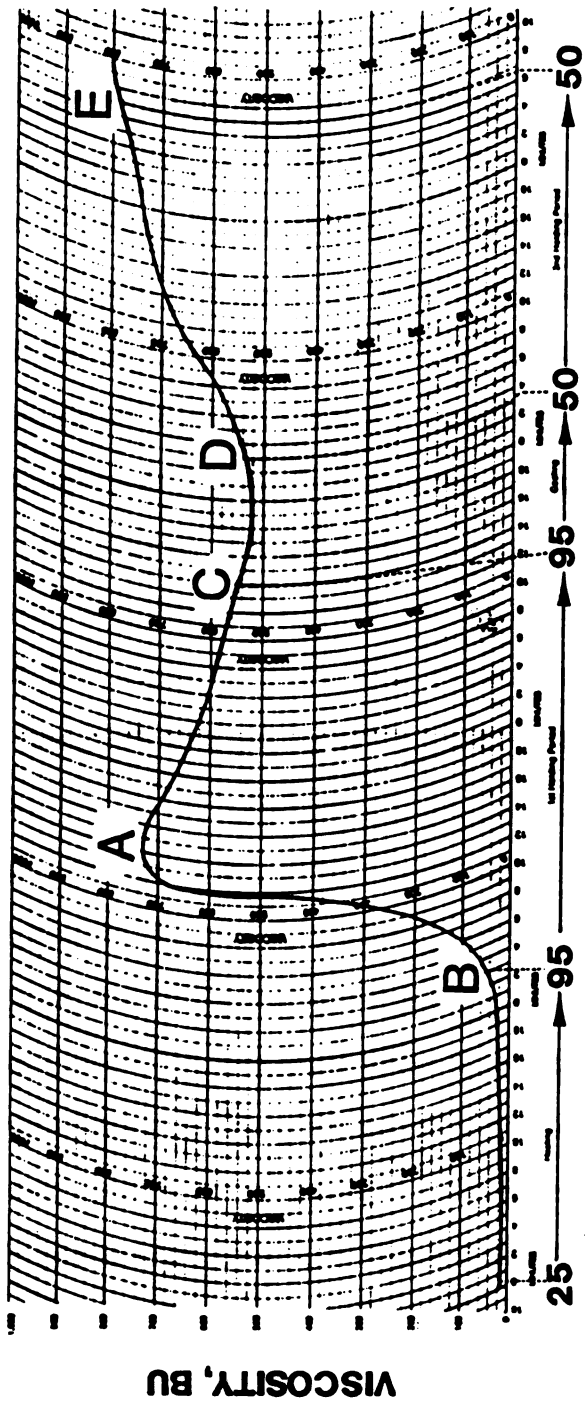


Figure 3. Points of significance on Brabender amylogram: A, peak (maximum) viscosity; B, viscosity of paste on attaining 95°C; C, viscosity at the end of 95°C cooking; D, viscosity of cooked paste after cooling to 50°C; E, viscosity at the end of 50°C holding.

swelling ability of starch and, hence, prevents the decrease in viscosity due to breakdown of highly swollen granules. During cooling the elements present in the hot paste tend to associate or retrograde. Therefore, the viscosity difference between point C and point D shows the tendency of retrogradation. Finally, the viscosity of the paste between point D and point E indicates the stability of the cooked paste in actual use.

Viscosity values corresponding to each significant point may be taken from the curve and plotted on linear coordinates against the logarithm of sample concentration as discussed by Mazurs et al. (1957).

The amylogram obtained from the Viscoamylograph reveals the viscosity changes of the starch-water system under a variety of controlled temperature conditions. These measurements have been used to derive a large amount of information that is useful to the cereal industry. This is also one of the reasons that this instrument has been so extensively used for routine quality control and some basic research applications.

Although the Viscoamylograph is commonly used for testing starch pasting properties, it can only run at low starch concentrations and the viscosities are not given in absolute units due to its complicated geometry. Moreover, it can only provide single-point determinations of viscosity values and does not measure yield stress.

Brabender viscograms are usually determined at an arbitrarily fixed starch paste concentration and the resulting peak viscosity and other values are used as criteria for starch characterization. A critical review of this method was made by Bhattacharya and Sowbhagya (1978). They reported that the current approach reveals a number of fallacies and suggested that starch characterization may be properly made not at a fixed paste concentration but at a fixed peak viscosity.

In contrast to the type of instrument mentioned above, rotational viscometers, with a simple and well-defined viscometer geometry, readily providing flow curves and absolute viscosity units, have become the single most widely used instruments for rheological determinations (Van Wazer et al., 1963). The most common type of rotational viscometer is the coaxial cylinder viscometer such as the Haake Rotovisco Viscometer.

The Rotovisco is a very versatile viscometer and can measure the apparent viscosity to an accuracy of 1% to 2%. The measuring head of the Rotovisco is activated through a 10-position geared transmission which is powered by a synchronous motor operating at 3000 rpm. A stress measuring device in the measuring head will transmit signals to the panel to give readouts. Shear stress is measured by a precision torsion spring which is interposed between the rotor in the sample fluid and the transmission cable. Thus, the viscous drag on the rotor is measured by the deflection of the torsion spring. This deflection is then measured by a potentiometer and the signal is recorded on the control panel with a range of 0 to 100 units. During measurement, a rotating body immersed in a liquid is subjected to a viscous drag, the magnitude of which (shear stress) depends on the speed of rotation (shear rate). The flow curve thus can be plotted as shear stress vs. shear rate (Van Wazer et al., 1963; Sherman, 1970). The viscosity and shear rate obtained is actually apparent viscosity and apparent rate of shear, respectively, since these terms have been derived from the Newtonian expression for rate of shear at the wall of the inner cylinder. Therefore, correction should be made to get the absolute values for non-Newtonian fluids (Van Wazer et al., 1963).

Due to the large variation of the scale and measuring system of different viscometers in obtaining starch rheological data, Kempf and

Kalender (1972) have urged the need for the standardization of suitable methods for comparisons of the test data from different instruments. The authors compared the precision and reproducibility of three viscometers. In the comparison of the Brabender Viscoamylograph and the Haake Rotovisco, they concluded that the Rotovisco, with a perforated paddle sensor, permitted exact measurement of rheological properties of starch and had better reproducibility. They criticized the heater design of the Viscoamylograph, indicating it did not provide uniform heat transfer which resulted in non-uniform homogenization of the starch paste, whereas the Rotovisco had better temperature control, effective homogenizing and less water evaporation.

Non-Newtonian Flow Behavior of Starch Pastes

Flow Models. Fluids following the simple Newtonian rheological model in which a linear relationship exists between shear stress (τ) and shear rate ($\dot{\gamma}$) can be expressed as:

$$\tau = \eta \, (\dot{\gamma}) \qquad (1)$$

where τ is shear stress (N/m^2), $\dot{\gamma}$ is shear rate (s^{-1}), and η is viscosity (Pa.s). In other words, Newtonian fluids maintain constant consistency irrespective of the velocity change.

Most of the fluid food products, however, do not follow this model and show deviation from Newtonian behavior. They are generally known as non-Newtonian. Holdsworth (1971) discussed this flow behavior and stated that it is often found for food products that the logarithmic plot of shear stress versus shear rate is linear over a wide range of shear rate. This empirical relationship is known as the power law and has been

used widely to characterize flow behavior of inelastic fluid materials. This equation can be written as:

$$\tau = K\ (\dot{\gamma})^n \qquad (2)$$

where τ is shear stress (N/m^2), $\dot{\gamma}$ is shear rate (s^{-1}), K is consistency index ($Pa.s^n$), and n is flow behavior index (dimensionless).

The consistency index generally increases with increased solid content of fluid viscosity. The flow behavior index is an indication of the departure from Newtonian fluid. When $0 < n < 1$, it is called pseudo-plastic (shear thinning) fluid in which the apparent viscosity decreases with increased shear rate. When $1 < n < \infty$, it is known as dilatant (shear thickening) fluid and the apparent viscosity increases with increased shear rate.

The power law model may be extended to include a yield stress value which is the force required to initiate flow. It is also known as Herschel-Bulkley model (Herschel-Bulkley, 1926):

$$\tau = K\ (\dot{\gamma})^n + \tau_y \qquad (3)$$

where τ_y is yield stress (N/m^2). Bingham plastic fluids are those which exhibit a yield stress initially and then behave as Newtonian fluids; they obey Equation 3 with $n = 1$. The above fluids discussed are all time-independent for which the shear rate is a function of shear stress only. Figure 4 shows the flow curves for model inelastic, homogeneous, incompressible, and time-independent fluids under isothermal conditions.

Some fluid materials whose shear rate is a function of both the magnitude and duration of the shear stress are known as time-dependent fluids. The shear stress of a thixotropic fluid decreases with time at a constant shear rate, whereas the shear stress of a rheopectic fluid

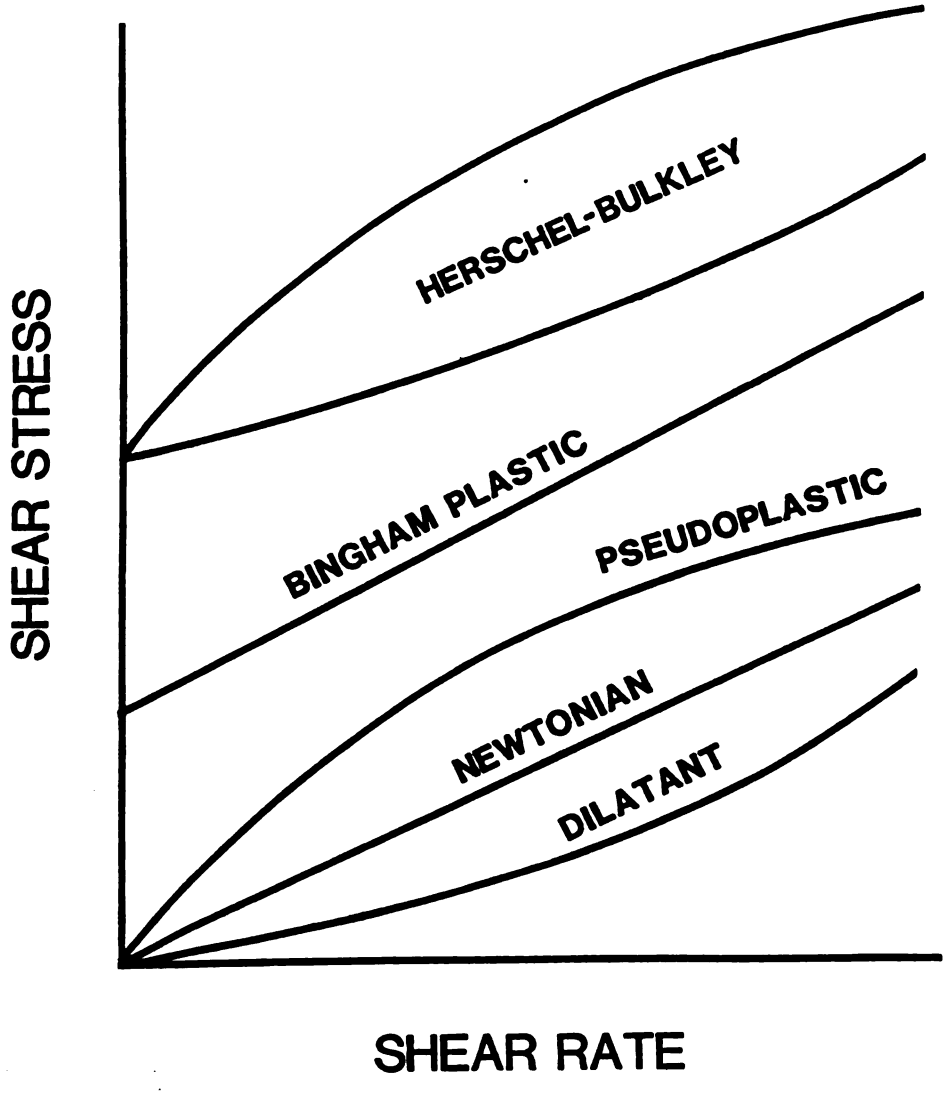


Figure 4. Flow curves for model inelastic, homogeneous, incompressible, and time-independent fluids under isothermal conditions

increases with time at a constant shear rate. This time-dependency can be measured with hysteresis loops or stress decay at constant rates as discussed by Van Wazer et al. (1963). A thorough review of the thixotropic materials was made by Mewis (1979).

Flow Behavior of Starch Pastes. Some starch dispersions showed dilatancy as reported by Williamson and Heckert (1931). When water is added to starch in the amount of 40% to 45%, the starch-water suspension becomes dilatant. It can flow easily at low shear rates but thickens drastically at high shear rates. Such dilatancy, or shear thickening, occurs in closely packed assemblage of solid particles, for which the system volume must increase to accomodate particle flow under shear. Morgan (1968) stated that this volumetric dilation will occur whenever the concentration of the spheric particles exceeds 52.3% (v/v) which is required for simple cubic packing. Hoffman (1972, 1974) also showed the dilatancy of dispersion of some polymeric particles with the volume fraction range of 0.46 to 0.60.

The flow behavior of wheat starch suspensions after cooking at various temperatures (60°C, 65°C, 70°C, and 75°C) for selected times (15 min, 30 min, 45 min, 60 min, and 75 min) was studied by Bagley and Christianson (1982). Viscosity for these cooked dispersions was determined with a Haake Rotovisco rotational viscometer at 60°C and 23°C. They reported that the cooked dispersions often showed dilatant behavior, particularly at the shorter cooking times, but always became a shear thinning (pseudoplastic) fluid at the longer cooking times. They concluded that if the particles, at the cooking range of 60°C to 75°C, are swollen enough by long cooking times so that flow can occur by deforming particles and thereby move by each other without volume

change, the viscosity will decrease with increased shear rate. However, if the particles are not so readily deformed as by long cooking times, or if the shear stress is too low to force the particles to deform and flow, then dilatancy will occur.

A study on the rheology of gelatinized starch suspensions of various starches was conducted by Evans and Haisman (1979). The starch suspensions were heated at 90°C and held to reach their maximum viscosity and then cooled to 60°C at which their flow behaviors were evaluated with a Haake Viscometer. The gelatinized paste was found to exhibit a pattern of a shear-thinning fluid whose flow curve fits the expression $\eta_{app} = K\dot{\gamma}^{m}$ over a wide range of low shear rates (0.0007 s^{-1} to 56 s^{-1}) and high shear rates (7 s^{-1} to 1142 s^{-1}). Behavior at very low shear rates indicates the existence of yield stress and can be expressed by $\tau = \tau_o + K\dot{\gamma}^{n}$. The apparent viscosity, flow behavior index, and yield stress are all concentration dependent. Evans and Haisman (1979) also concluded that significant viscosity effects occur only above a threshold concentration corresponding closely to the point at which the flocculated swollen granules just fill the total volume of the system.

Another rheological property found in the starch paste is thixotropy. The apparent viscosity of thixotropic fluid decreases with increased time at a constant rate of shear. Mackley (1937) reported that 300 g of wheat starch in 213 cc of distilled water showed the thixotropic behavior tested by Farinograph.

Niihara and Matsumoto (1981) reported that the apparent viscosity of starch paste after gelatinization measured by a cone-plate viscometer decreased markedly and approached an equilibrium due to thixotropic breakdown of the macroscopic sample structure. The structural breakdown,

however, was not completely recovered after resting as could be seen from the different shapes of flow curves of the repeated measuring cycles.

Odigboh and Mohsenin (1974), using the McMichael Viscometer, noted that cassava starch paste was characterized as a plastic fluid, and shown to possess an appreciable shear thinning tendency. After the paste had been sheared for some time, no further breakdown occurred and paste became shear-independent. Since this breakdown is irreversible, the paste is said to show rheomalaxis.

MATERIALS AND METHODS

Production of Flour Fractions

Source of Beans

Prime handpicked navy beans (*Phaseolus vulgaris*), from the Wolverine Bean Division, Bay City, Michigan, provided by the Michigan Bean Shippers Association, were used in the production of flour fractions. These beans were shipped to the Food Protein Research and Development Center at Texas A & M University for processing.

Roasting, Milling, and Air-Classification

Beans were dry-roasted in a particle-to-particle heat exchanger which consisted of two metallic drums with variable rotational speed and inclination to control product residence time (Figure 5). Heat transfer media was heated in the lower drum by a gas flame, transported to the upper drum where it was mixed with beans. Beans were then roasted by intimate contact with hot media while traveling through the drum with agitation of the bed by parallel baffles. The heat transfer media was type A 90% aluminum oxide ceramic beads with a diameter of 1/16 in and a specific gravity of 3.6. At the end of the upper drum, the media and beans were separated by a screen, with the media being returned to the lower drum and the heated beans discharged from the system.

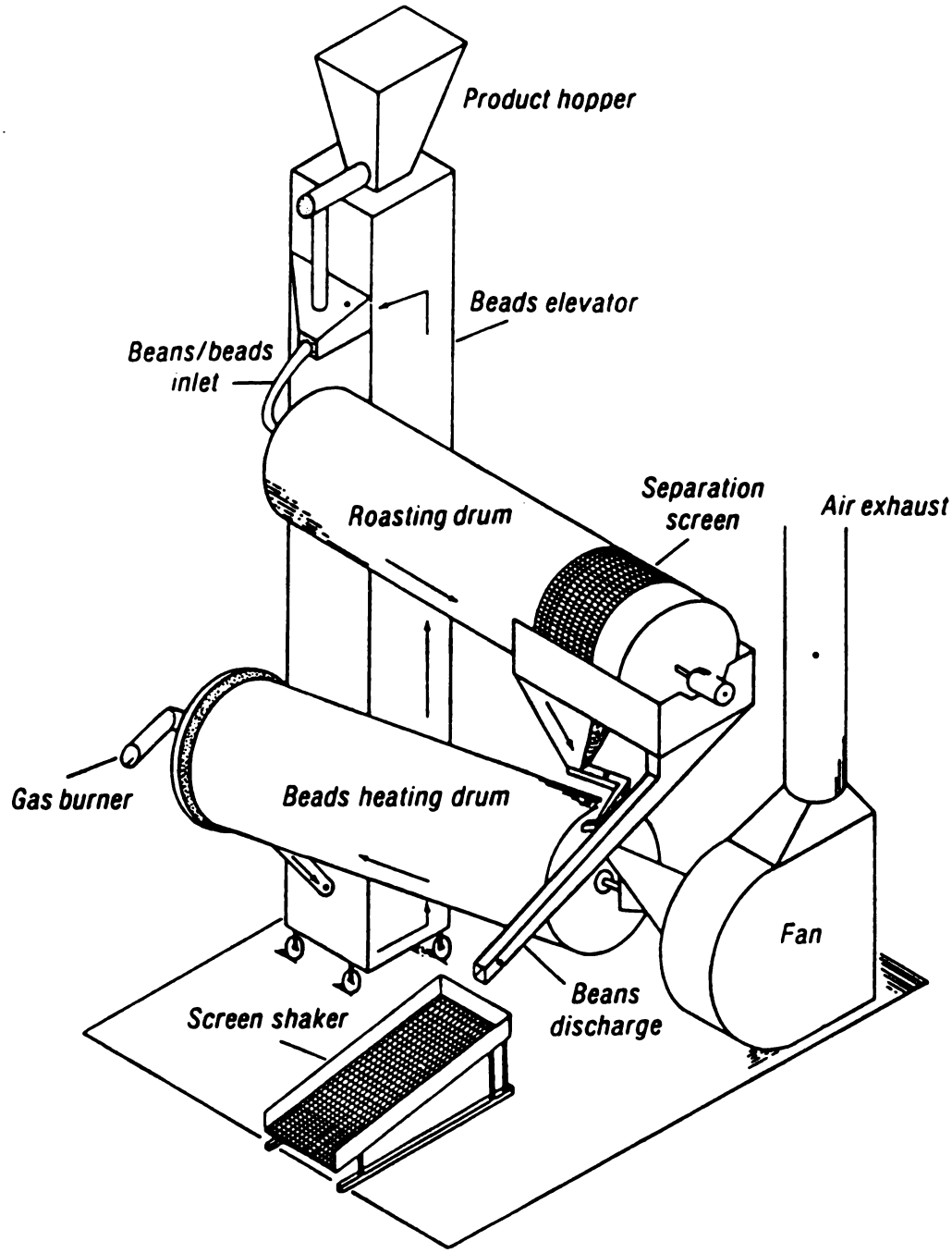


Figure 5. Schematic diagram of the particle-to-particle heat exchanger (Source: Aguilera et al., 1982a)

The flour fractions were obtained from navy beans roasted in the heat exchanger with bead temperature of 240°C and 270°C for one and two minutes at the bean-to-bead ratio of 1/10 and 1/15 (Aguilera et al., 1982a). Further grinding of these roasted beans and separation of bean flours were also performed at Texas A & M University.

Roasted whole navy beans were cracked in a disc attribution mill (Bauer Bros. Co., Springfield, OH) and hulls removed by aspiration. Roasted whole beans and hulls were ground in a swinging blade Model D_6 Fitzmill (W.J. Fitpatrick Co., Chicago, IL) to produce whole flour and hull flour. Cracked cotyledons were finely ground in an Alpine Kolloplex Model 1602 stud impact mill (Alpine American Corp., Natick, MA) at 11,500 rpm. Ground flours were air-classified to produce fine (F1) and coarse (C1) fractions. The coarse fraction was remilled, air-classified into fine (F2) and coarse (C2) fractions. High protein flour was the combination of F1 and F2 fractions and high starch flour was the C2 fraction (Aguilera et al., 1982b). Air-classified flour fractions obtained from beans which underwent specific roasting treatments were used in Studies 1 and 2. The procedures for the production of bean flour fractions are presented in Figure 6.

Based on the data reported by Uebersax et al. (1980), the air-classified flour fractions, obtained from navy beans roasted at 240°C for one minute at the bean-to-bead ratio of 1/15 (final bean temperature: 113°C), possessed the most desirable color and nitrogen solubility and therefore were studied for their physicochemical characteristics in Study 1.

In order to investigate the effect of roasting of beans on the quality of flour fractions under various storage conditions, flour fractions obtained from navy beans roasted at 240°C and 270°C for

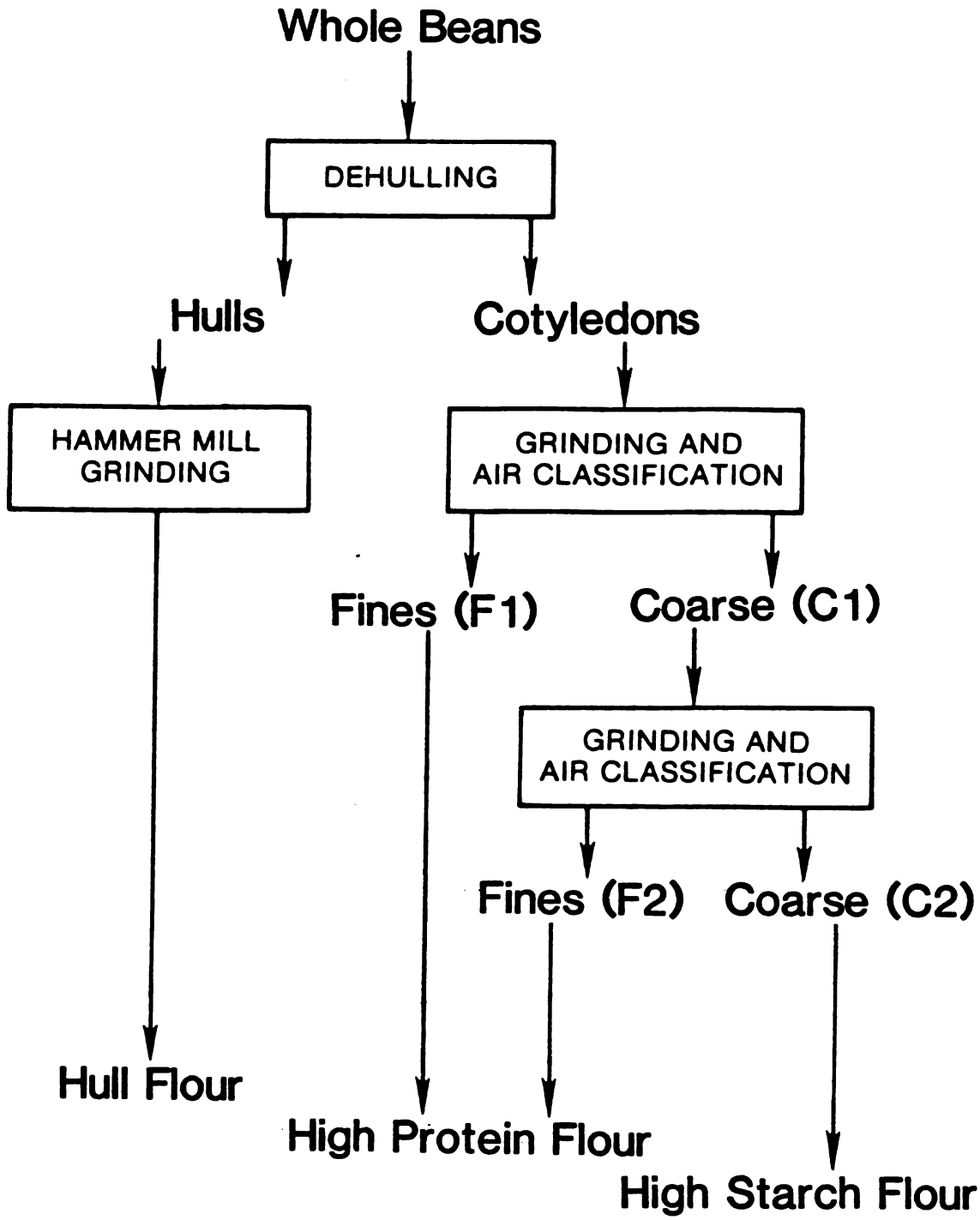


Figure 6. Flow diagram for the production of navy bean flour fractions used in Studies 1 and 2

one and two minutes at the bean-to-bead ratio of 1/15 were used in Study 2.

In the Study 3, the flour fractions were produced from navy beans roasted in the heat exchanger with a bead temperature of 240°C for one minute at the bean-to-bead ratio of 1/15. Roasted beans were cracked through a corrugated roller mill (Ferrell Ross, Oklahoma City, OK) and the hulls were then removed in a zig-zag aspirator (Kice Metal Products, Wichita, KS). The cracked cotyledons were sent to Alpine American Corp., Natick, MA, and were ground into fine flour with a stud impact mill Model 250 CW (Alpine American Corp., Natick, MA). This fine flour was further separated in a Model 410 MPVI air-classifier (Alpine American Corp., Natick, MA) to obtain coarse (C1) and fine (F1) fractions. The fine fraction (F1) was reclassified to obtain coarse (C2) and fine (F2) fractions. Thus, three fractions were produced from these dry roasted navy beans. Figure 7 shows the process sequence for the production of bean flour fractions. The C2 starch fraction was further processed to obtain purified starch for use in Study 3.

Purification of High Starch Flour

The high starch flour obtained from air-classification was further purified to produce starch using wet processing according to the method described by Naivikul and D'Appolonia (1979), with some modification. Approximately 5 kg of air-classified high starch flour (C2) were extracted with 20 kg 0.016 N NaOH solution by constant stirring for 20 min. High starch flour was then partially purified by centrifugation (2,000 rpm) for 20 min. Further purification of the starch was achieved by washing the crude starch three times with distilled-deionized water, two times with 70% ethanol, and two additional times with distilled-

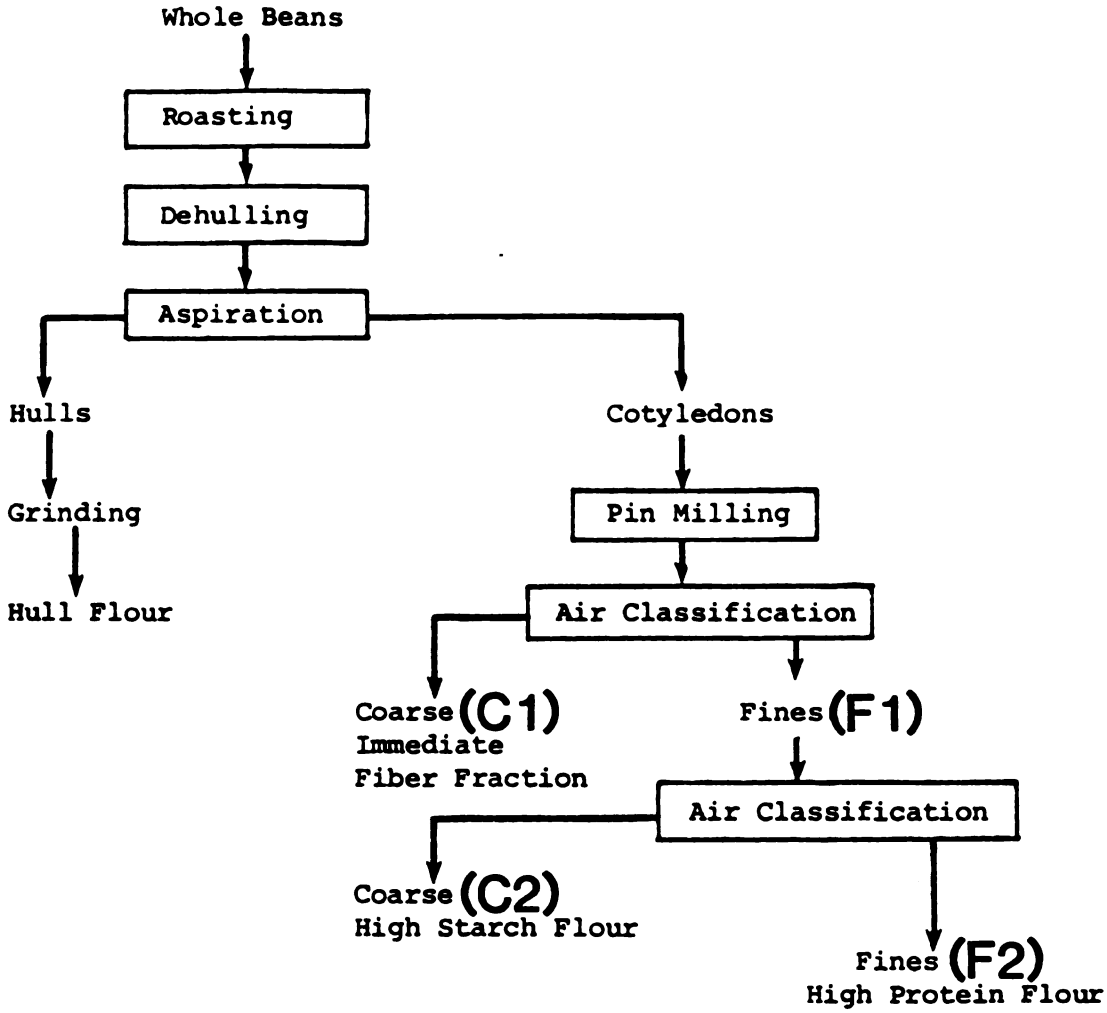


Figure 7. Flow diagram for the production of navy bean flour fractions used in Study 3

deionized water. After each washing step, the supernatant and sludge were discarded and only the good starch in the bottom of the centrifuge tube remained. The prime starch was then air-dried in an oven (about 38°C) for 48 hr and ground into flours using a Waring blender operated at low speed. This purified navy bean starch was then studied for its gelatinization and rheological properties.

Experimental Procedures

Study 1: Physicochemical Characteristics of Dry-Roasted Navy Bean Flour Fractions

Navy beans were dry-roasted in a particle-to-particle heat exchanger with a bean temperature of 240°C for one minute at the bean-to-bead ratio of 1/15. Roasted navy beans were dehulled by air aspiration, pin-milled, and air-classified to yield whole, hull, high protein, and high starch flour fractions.

Yield, proximate analysis, color, enzyme neutral detergent fiber (ENDF), starch, nitrogen solubility indices, and oligosaccharide contents of these flour fractions were determined. Physical dough properties of dry-roasted navy bean flour fractions (whole flour, hull flour, high protein flour) were evaluated with the Brabender Farinograph. Standard wheat flour was tested for comparison. Pasting characteristics of dry-roasted navy bean whole flour and the high starch fraction were determined in a Brabender Viscoamylograph. Corn starch was also evaluated for its pasting characteristics as a comparison.

Study 2: Effect of Roasting and Storage Conditions on the Stability of Air-Classified Navy Bean Flour Fractions

Navy beans were dry-roasted in a particle-to-particle heat exchanger with bead temperatures of 240°C and 270°C for one minute and two minutes at the bean-to-bead ratio of 1/15. Roasted navy beans were dehulled by air aspiration, pin-milled, and air-classified to yield whole, hull, high protein, and high starch flour fractions. These flours were sealed in polyethylene bags and stored at 4°C until used. Two experiments were conducted to study the storage stability of flour fractions.

The first experiment was designed to evaluate the quality change of flours as affected by roasting treatment of dry beans and water activity during short term storage.

Flour samples were stored at 20°C under eight selected relative humidities in static desiccators over appropriate saturated salt solutions (Rockland, 1960). Prior to placement of the samples in these desiccators, saturated salt solutions had developed and maintained various levels of relative humidity or water activity (a_w) as follows: KNO_2 (0.48 a_w), $Mg(NO_3)_2$ (0.55 a_w), $NaNO_2$ (0.64 a_w), NaCl (0.75 a_w), $(NH_4)_2SO_4$ (0.80 a_w), KCl (0.86 a_w), KNO_3 (0.92 a_w), and K_2SO_4 (0.97 a_w). Duplicate flour samples of about 10 g each of the navy bean fractions were placed in small aluminum pans and were allowed to equilibrate with the controlled a_w's. Approximately eight weeks were needed for equilibration. Initial moisture contents of the samples were determined prior to storage. At the end of each week throughout the storage period, water uptake of the flours as determined by moisture measurement was recorded. The mold growth was visually estimated using a 10 point scale of mold coverage on the surface of the flour samples (0 = 0% and 10 = 100%). The final

equilibrium moisture content, expressed in both dry weight (db) and wet weight (wb) basis, was recorded for each sample so that asorption isotherms could be drawn. After eight week storage, the equilibrated bean flour fractions were sealed in 50 ml glass vials and held at 4°C until used. Quality characteristics of color, nitrogen solubility index, sugar level, and starch content were evaluated.

The flour fractions produced from beans with the optimum roasting treatment, as confirmed in the first experiment of this study, were used in the second experiment.

Flour fractions from this roasting treatment (roasting time, one minute; roasting temperature, 240°C; bean-to-bead ratio, 1/15) were equilibrated in a moisture controlled chamber overnight to obtain final moisture contents of 6%, 9%, and 12% db. These flours were then hermetically sealed in duplicate 303 x 406 metal cans and stored in controlled temperature rooms of 20°C and 37.7°C. Color, nitrogen solubility indices, and 2-thiobarbituric acid (TBA) values for these flour samples were determined after 12 and 24 month storage.

Study 3: Gelatinization and Rheological Properties of Purified Navy Bean Starch Pastes

Navy beans were dry-roasted in a particle-to-particle heat exchanger with a bead temperature of 240°C for one minute at the bean-to-bead ratio of 1/15. Roasted whole beans were cracked and dehulled in an air-aspirator. The cracked cotyledons were pin-milled, air-classified to yield coarse and fine fractions. The fine fraction was reclassified to obtain high protein and high starch flours. This high starch flour was further processed to obtain bean starch of high purity. Proximate composition of the starch was determined.

The study was designed to investigate, using a computer-assisted Haake Rotovisco Viscometer, the effect of starch concentrations (6%, 8%, 10%, and 12% db) and cooking temperatures (75°C, 85°C, and 95°C) on the gelatinization and rheological properties of hot pastes. The rheological property of cooled pastes at 50°C was also determined to assess the retrogradation tendency and stability of the starch. Figure 8 shows the flow diagram of the experimental procedures employed in this study. Three replications were run for each treatment throughout the experiment.

For each test, weighed amounts of starch were added gradually into a bowl containing 100 ml of distilled water and thoroughly mixed to achieve a suspension of desired concentration on a dry weight basis. This suspension was then immediately poured into a cylindrical stainless steel Haake MV cup until the lower ring mark on the inside wall of the cup was reached. The above procedures were performed at room temperature (25°C).

The MV cup was then loaded into the temperature vessel which had reached and maintained the desired cooking temperature, and had the perforated paddle mixer and protective lid ready. This protective lid covered the sensor system and effectively deterred water evaporation when tests were being run at high temperatures.

The digital counter of the basic unit was fine tuned to read zero point with a blinking "-" and the speed on the speed programmer was set at 50 rpm which provided minimum shear with sufficient mixing to maintain suspension of starch granules. As soon as these steps were taken, the paddle mixer was turned on and the starch suspension was stirred for up to 60 min to become paste. The swelling response and

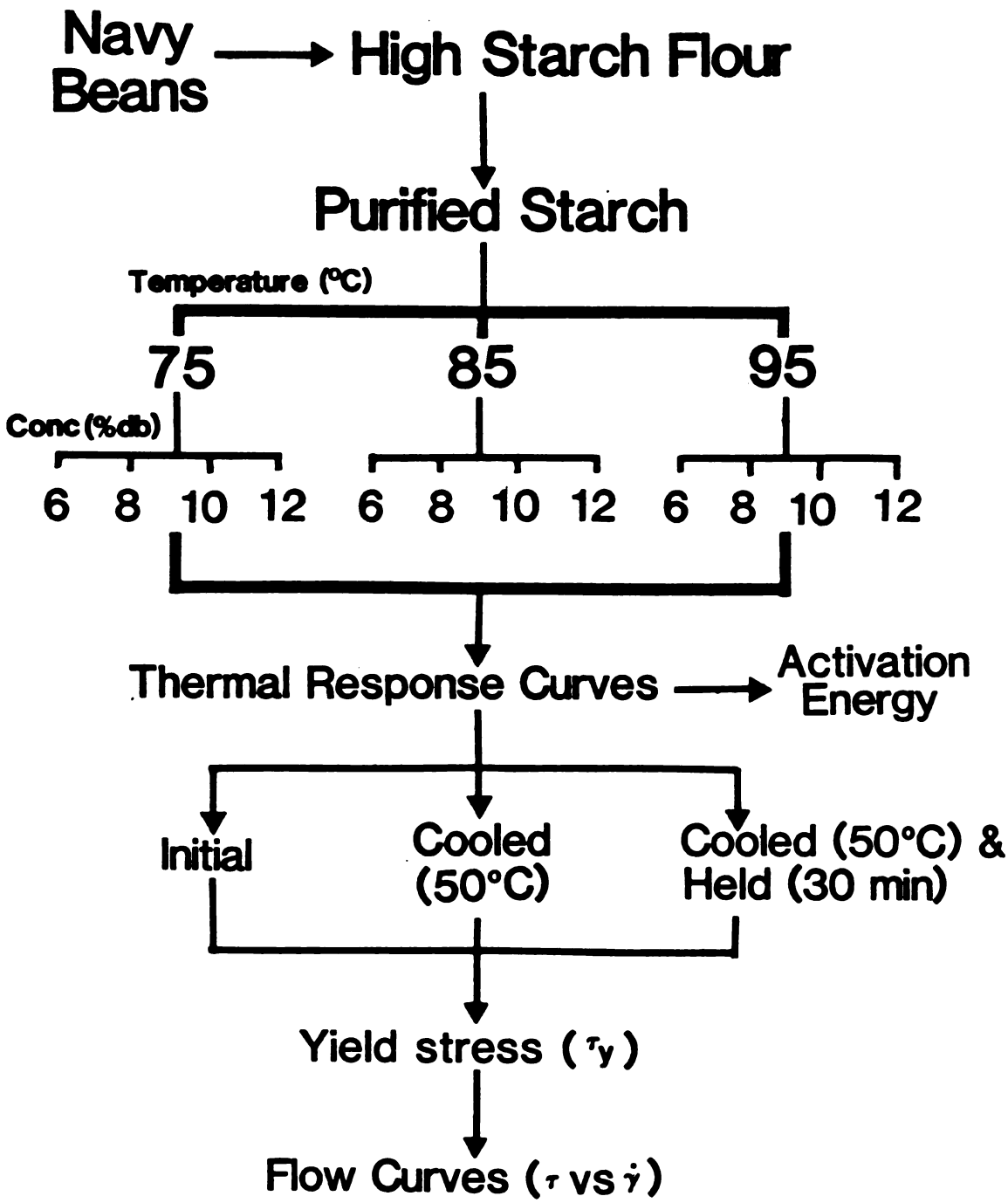


Figure 8. Flow diagram of the experimental procedures for the study of gelatinization and rheological properties of purified navy bean starch pastes

shear breakdown (if any) of the starch paste were recorded to obtain a torque-time curve.

Temperature profile of the starch paste during heating was recorded by inserting a thermocouple into the paste in the preliminary test. It was found that temperature increased rapidly to the desired cooking temperature in about five minutes for all three temperatures (75°C, 85°C, and 95°C) at various concentrations and was maintained at that level with ±0.5°C for the entire cooking period.

After 60 min of cooking, the paddle mixer was replaced with the MV 1 bob which had equilibrated in a hot water bath at that cooking temperature. The starch paste, while still maintained at the cooking temperature, had been left for one minute before the yield stress determination actually started. The rotational speed was programmed to increase linearly from 0 to 1 rpm (corresponding to a shear rate of approximately 2.5 s^{-1}) in 60 sec and to decrease linearly back to 0 rpm in another 60 sec. The torque values of this shear cycle, recorded as torque-rotation speed, were transformed into shear stress values. The yield stress (or yield value) was the average of the two intercepts on the shear stress (Figure 9).

Flow data were measured after yield stress determination by recording the torque values with increased rotor speed. Torque values were measured at the manually set speeds from 1 to 100 rpm with 12 increments, each increment requiring 10 sec for measurement. The computer program in the Hewlett-Packard system was written such that a five second period was held for reaching steady state condition and another five seconds were used for taking 10 torque readings before the next higher speed was selected.

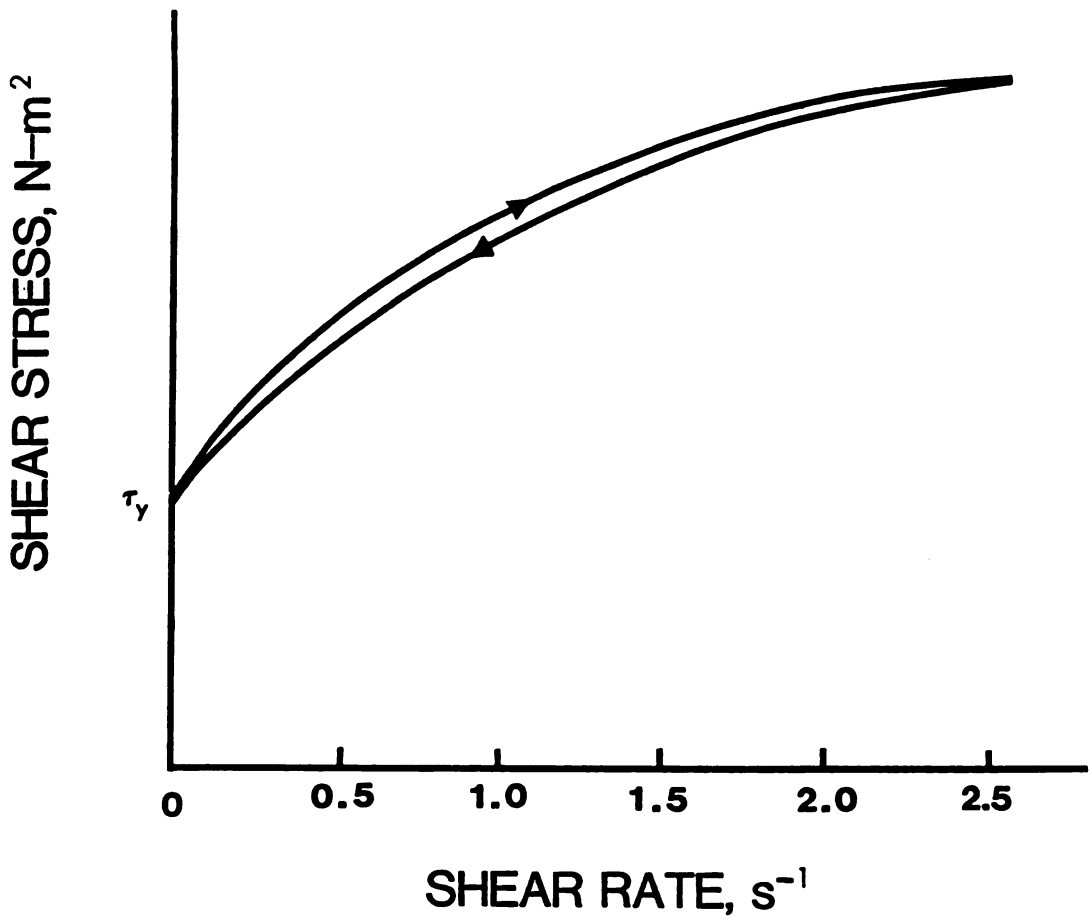


Figure 9. Determination of yield stress for navy bean starch paste with one shearing cycle

Ten torque readings were averaged for each speed increment and the torque-rpm readings were converted to shear stress and shear rate, respectively, as discussed under the section of the calculation of shear stress and shear rate.

For cooled paste measurements, the sample preparation and cooking procedures were repeated, and the paddle mixer was replaced with the MV 1 bob as described previously. The starch pastes were then cooled to 50°C by circulating cool water through the temperature vessel with a predetermined faucet opening at the paste cooling rate of 1.5°C/min. Yield values and flow curves of the cooled pastes were determined as discussed earlier.

The same procedures and measurements were performed again on samples except that the starch pastes were cooled and held for additional 30 min prior to the rheological study. This additional holding provided a practical measurement for extended stability as may be found under production system.

Chemical and Physical Analyses of Flour Fractions and Starch

Standard approved methodology was used to evaluate the chemical composition and physical and functional properties of bean flour fractions and starch (AACC, 1962).

Moisture

Approximately 5 g of bean flour fractions or bean starch were weighed into previously dried and tared crucibles and dried to a constant weight at 80°C for 24 hr in an air-oven. Percent moisture was determined from the weight loss on the fresh weight basis (AACC Method 44-15):

$$\% \text{ Moisture} = \frac{\text{moisture loss (g)}}{\text{sample fresh wt (g)}} \times 100$$

Ash

Dried samples obtained from the above moisture determination were placed in a muffle furnace and incinerated at 525°C for 24 hr. The uniform white ash was cooled in a desiccator and weighed at room temperature. Percent ash was determined on the dry weight basis (AACC Method 08-01):

$$\% \text{ Ash} = \frac{\text{residue wt (g)}}{\text{sample dry wt (g)}} \times 100$$

Protein

Approximately 30 mg of bean flour fractions or bean starch were weighed and anlyzed by the standard Micro-Kjeldahl procedure. Percent nitrogen was then multiplied by 6.5 to obtain % total protein (AACC Method 46-13):

$$\% \text{ Total Protein} = \% \text{ nitrogen} \times 6.25$$

Nitrogen Solubility Index (NSI)

Approximately 5 g of bean flour fractions were weighed into a 400 ml beaker and thoroughly mixed with 200 ml distilled water. The mixture was stirred at 120 rpm with a mechanical stirrer for 120 min at 30°C. The mixture was then centrifuged and filtered through glass wool to obtain clear liquid. Percent water-soluble nitrogen was determined from

the liquid using AACC Method 46-13. Nitrogen solubility index, expressing water soluble nitrogen as a percentage of the total nitrogen, was calculated (AACC Method 46-23):

$$NSI = \frac{\% \text{ water-soluble nitrogen}}{\% \text{ total nitrogen}} \times 100$$

Fat

Approximately 2 g of bean flour fractions or bean starch were dried to a constant weight in a vacuum oven at 95°C to 100°C prior to placement in a Whatman cellulose extraction thimble. The thimble was then placed in a Soxhlet extractor, refluxed with about 300 ml hexane for 6 hr to remove flour lipid. A 50 ml aliquot of the filtrate, obtained by filtering the cooled hexane through a fine glass crucible, was dried to calculate the crude fat content (AACC Method 30-26):

$$\% \text{ Crude Fat} = \frac{\text{fat wt (g)} + \text{flask wt (g)} \times \text{filtrate vol (ml)}}{\text{sample dry wt (g)} \times 50 \text{ (ml)}} \times 100$$

Enzyme Neutral Detergent Fiber (ENDF)

Bean flour fractions were evaluated for ENDF by the method described by Robertson and Van Soest (1977). This method was modified to include 1 mg of amyloglucosidase to provide additional digestion of starch.

Sugars

Extraction. Sugars were analyzed by first extracting a 1 g flour sample with 10 ml of 80% ethanol in an 80°C water bath shaker for 10 min. The mixture was centrifuged at 2000 rpm for three minutes and the supernatant was collected into a new tube. The extraction was repeated two

more times with the same procedure except that 5 ml of 80% ethanol were used the second time. It was found, from the preliminary experiments, that the combination and order of this 80% ethanol solvent extraction procedure (i.e., 10 ml, 5 ml, and 10 ml) resulted in maximum sugar values. The precipitate was saved for starch analysis. Two ml of 10% lead acetate were added to the extract collected from these three extractions. The mixture was shaken and centrifuged (2000 rpm, 3 min) to precipitate protein; the supernatant was transferred to another tube. Two ml of 10% oxalic acid were added to the tube and again the mixture was shaken and centrifuged to remove the residual lead acetate. The final supernatant was brought to 25 ml volume and passed through a SEP-PAK cartridge (Waters Associates, Inc.) prior to injection into a High Performance Liquid Chromatograph.

High Performance Liquid Chromatography (HPLC) Analysis. The HPLC consisted of a Solvent Delivery System 6000A, a Universal Chromatograph Injector U6K, Differential Refractometer R401, and a Data Module Model 730 (Waters Associates, Inc.). Acetonitrile-water (75:25, v/v); pH 4.0) was used as the solvent at a flow rate of 2.5 ml/min. The Carbohydrate Analysis (μBONDAPAK) column (Waters Associates, Inc.) was used to resolve the sugars from the aqueous extract. Figure 10 represents the resolution curves for the sugars detected in flour samples. Quantitation and identification of sugars were done using the external standard method programmed in the Data Module to calculate the absolute amounts of the components in the injected sample (30μl) and to obtain the percent sugar content based on dry flour weight. Percent sugar in the flour sample was calculated according to the following formula:

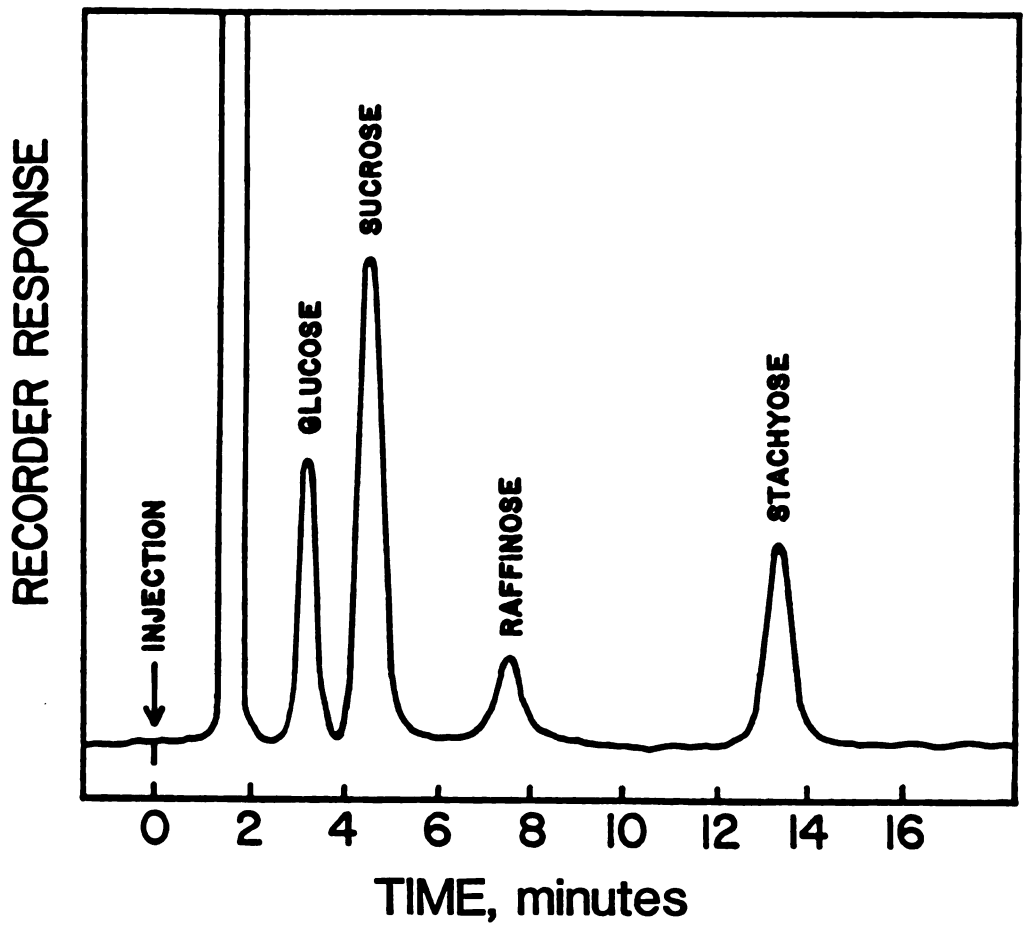


Figure 10. Elution pattern of HPLC sugar analysis of dry-roasted navy bean flour fractions

$$\% \text{ Sugar} = \frac{\text{Data Module sugar (mg/ml)} \times \text{injected sample volume (ml)}}{\text{sample wt (mg)}} \times 100$$

Starch

Aliquot Preparation. The precipitate obtained from the sugar extraction was air dried to remove ethanol which could interfere with the enzyme activity and cause an inaccuracy in starch determination. The dried pellet was transferred to a 250 ml centrifuge tube and then dissolved completely with 50 ml 0.5 N NaOH solution. The slurry was then neutralized by adding 50 ml of 0.5 N acetic acid and centrifuged at 1500 rpm for three minutes to obtain the supernatant.

Enzyme Solution Preparation. Two volumes of 0.2 M acetic acid were mixed with three volumes of 0.2 M sodium acetate to form the 0.2 M acetate buffer stock solution which was stored under refrigeration in a brown colored bottle. The α-amylase solution was prepared by mixing 200 mg of α-amylase with 100 ml of 0.2 M acetate buffer solution. The amyloglucosidase solution was prepared by mixing 500 mg of amyloglucosidase with 100 ml of 0.2 M acetate buffer solution. These enzyme solutions were used immediately after preparation.

Assay. A 0.4 ml sample size of the supernatant was hydrolyzed in 1.8 ml α-amylase solution (2 mg/ml) for one hour and in 1.8 ml amyloglucosidase solution (5 mg/ml) for an additional hour. The hydrolysis was performed in a test tube which was shaken in a 55°C warm water bath. The hydrolyzed sample (25μl) was injected into the YSI Model 27 Industrial Analyzer (Yellow Springs Instrument Co., Inc.) to assay for starch.

HunterLab Color Values

The HunterLab Model D25 Color and Color Difference Meter standardized with a white tile (L=95.35, a_L=-0.6, b_L=+0.4) was used to evaluate the color of bean flours. A 100 g sample of bean flour was placed in an optically inert glass cylinder cup and covered with an inverted, white lined can to keep out extraneous light.

Mixing Properties of Dough

Physical properties of doughs made from the dry-roasted navy bean whole flour, hull flour, and high protein flour were evaluated with the Farinograph (Brabender Instruments, Inc.) equipped with a 50 g bowl. The constant dough weight procedure of the AACC Method 54-21 was followed with a 50 g sample composed of 10% bean flour and 90% wheat flour. Wheat flour was used as a standard for comparison.

Pasting Characteristics of Starch

Pasting properties of dry-roasted whole navy bean flour and high starch fractions were determined by AACC Method 22-10 in a Brabender Viscoamylograph (Brabender Instruments, Inc.) equipped with a 700 cm-g sensitivity cartridge. Whole flour or high starch flour (67.5 g) was suspended in 450 ml of distilled water and poured into the amylograph bowl. The temperature of the flour suspension was raised uniformly from 54°C to 95°C, held at 95°C for 15 min, and then cooled uniformly for 16 min to a final temperature of 71°C. The heating and cooling rates were 1.5°C/min. Corn starch was also tested for comparison.

2-Thiobarbituric Acid (TBA)

TBA number defined as mg of malonaldehyde per 1000 g of sample was determined with the method described by Tarladgis et al. (1959) to evaluate fatty acid oxidation in stored flours. A 5 g flour sample was mixed with 48 ml distilled water and 2 ml HCl solution prior to distillation. Five ml of the distillate were collected and mixed with 5 ml TBA reagent. The mixture was heated in a boiling water bath for 35 min. A distilled water-TBA reagent blank was also prepared. The mixture was then cooled in tap water, transferred to an envette for the reading of its optical density against the blank at a wavelength of 538 nm. TBA number was calculated by multiplying the reading by the factor 7.8.

Test Apparatus for Rheological Measurements

The Haake Viscometer system (Haake Inc., Saddle Brook, NJ) used in the third study consisted of a basic unit Rotovisco RV12, a speed programmer PG142, a measuring drive unit M500, an MV1 sensor system with a temperature vessel, and a constant temperature bath and circulator F3-C. The Hewlett-Packard 85 computer with a 3497A Data Acquisition/ Control unit was interfaced to the basic unit to facilitate data collection.

Although temperature control was rated good as suggested by Van Wazer et al. (1963), some heat loss during the transportation of hot water was evident. The settings of the temperature control unit to give various test temperatures, therefore, were predetermined for accuracy and reproducibility. By trial and error, the settings on the

temperature control unit were found to be 76.5°C for 75°C, 87°C for 85°C, and 97°C for 95°C.

The measuring drive unit M500 measured the torque values ranging from 0 to 0.0049 N-m (0.00049 N-m/unit reading). A schematic illustration for the MV1 sensor system is shown in Figure 11. The perforated paddle mixer was employed to stir the starch suspensions in the MV cup during cooking. The torque response of the starch gelatinization, thus, could be recorded. The MV1 bob was used to determine the rheological properties of hot and cooled starch pastes.

Calculations of Shear Stress and Shear Rate

Theory of Coaxial Cylinder Viscometer

The Coaxial Cylinder Viscometer is composed of two distinct parts: inner cylinder (bob) and outer cylinder (cup), as shown in Figure 11 (b). A bob of radius R_b is suspended to the level of h in the liquid which is held in the cup of radius R_c. A distance of L is noted to separate the bottom of the cup to that of the bob. As the bob rotates at an angular velocity of Ω, a viscous drag results from the resistance of liquid flow. A general equation for this relation is:

$$\dot{\gamma} = - d\nu/d\gamma = f(\tau) \qquad (4)$$

$\dot{\gamma}$ = rate of shear

τ = shear stress

To study the flow of fluid and the relationship between shear stress and rate of shear between two vertical coaxial cylinders, certain assumptions have to be made in order to arrive at the fundamental

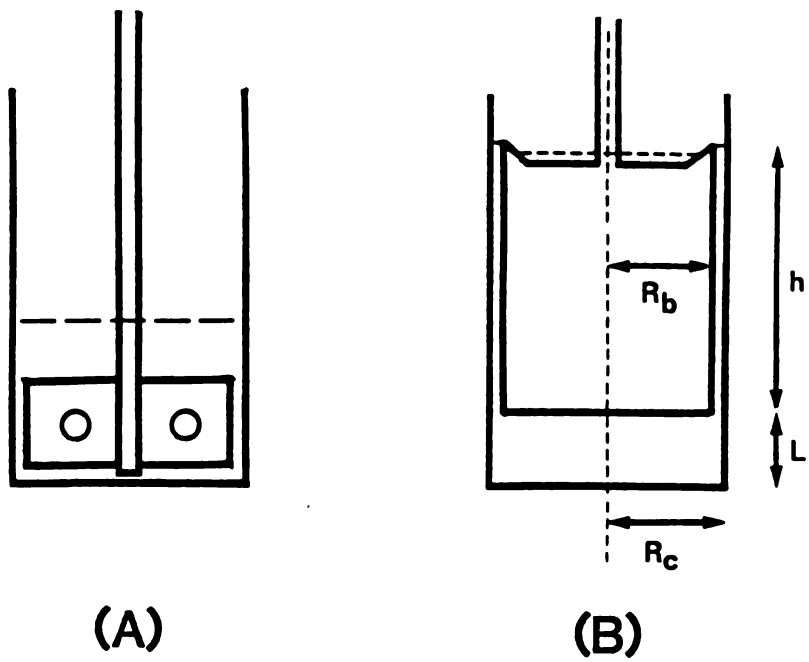


Figure 11. Schematic illustration for MV1 sensor system of the Haake Rotovisco Viscometer: A, perforated paddle mixer; B, bob

equations used for deriving various equations for specific fluid models. These restrictions assume that the system has:

(1) incompressible fluid,

(2) steady-state laminar flow,

(3) non-slip condition,

(4) two-dimensional motion, and

(5) isothermal condition

Shear Stress

Setting up the viscous flow problem by simplifying the equations of change in the cylindrical coordinates, one needs an equation of continuity, equation of motion, and initial and boundary conditions (Bird et al., 1962). The equation of continuity in cylindrical coordinates is:

$$\partial\rho/\partial\theta + (1/\gamma)(\partial[\rho\gamma v_\gamma]/\partial\gamma) + (1/\gamma)(\partial[\rho v_\phi]/\partial\phi) + \partial(\rho v_z)/\partial z = 0 \quad (5)$$

Since $v_\gamma = \gamma_z = 0$ and ρ being a constant from the assumptions, Equation 5 is reduced to:

$$(\rho/\gamma)(dv_\phi/d\phi) = 0 \quad (6)$$

and v_ϕ turns out to be a constant.

The equation of motion for steady state with the restrictions cited above is therefore reduced to:

$$(1/\gamma^2)\, d\,(\gamma^2\tau_{\gamma\phi})/\, d\gamma = 0 \quad (7)$$

This may be integrated to give:

$$\tau_{\gamma\phi}\,\gamma^2 = C_1 \quad (8)$$

With the bob rotating at an angular velocity of Ω, the measured torque at the outer cylinder is M, then

$$M = \tau_{\gamma\phi}\Big|_{\gamma = R_c} \cdot 2\pi \cdot R_c \cdot h \cdot R_c \tag{9}$$

Hence, $C_1 = M/2\pi h$ and

$$\tau = M/2\pi h\gamma^2 \tag{10}$$

The above expression is good for any fluid and can also be obtained by knowing that angular momentum must be transmitted undiminished from the outer cylinder to the inner one.

Shear Rate

Under laminar flow the velocity gradient at a distance γ from the axis of rotation, with angular velocity of ω, is

$$\frac{dv}{d\gamma} = \gamma \frac{d\omega}{d\gamma} \tag{11}$$

From Equation 4 and 11

$$-\gamma\frac{d\omega}{d\gamma} = f(\tau) \tag{12}$$

Taking the derivatives of γ with respect to τ from Equation 10, the following equation may be obtained:

$$\frac{d\gamma}{\gamma} = -\frac{d\tau}{2\tau} \tag{13}$$

so that

$$d\omega = \tfrac{1}{2} f(\tau) \frac{d\tau}{\tau} \tag{14}$$

Integrating Equation 14 from the bob, where $\omega = \Omega$ and $\tau = \tau_b$, to the cup, where $\omega = 0$ and $\tau = \tau_c$, gives

$$\Omega = \tfrac{1}{2} \int_{\tau_b}^{\tau_c} \frac{f(\tau)}{\tau} \, d\tau \tag{15}$$

The exact solution for the shear rate at R_b for an unknown fluid may be found (Krieger, 1968):

$$\dot{\gamma}_b = \frac{2\,\Omega\alpha^{2/m}}{m(\alpha^{2/m}-1)} \left\{ 1 + m^2\, m'\, f \left(\frac{2 \ln \alpha}{m} \right) \right\} \tag{16}$$

where $\alpha = R_b / R_c$ (17)

$$m = \frac{d \ln \tau_b}{d \ln \Omega} = \frac{d \ln \tau}{d \ln \Omega} \tag{18}$$

$$m' = \frac{d\,(1/m)}{d \ln \tau_b} = -\frac{1}{m^2} \frac{dm}{d \ln \tau} = -\frac{1}{m} \frac{d \ln m}{d \ln \tau} \tag{19}$$

and $$f(x) = \frac{x\,(e^x [x-2] + x + 2)}{2\,(e^x - 1)^2} \tag{20}$$

Flow Models and Calculations of Rheological Parameters

The power law model (Equation 2) and Herschel-Bulkley model (Equation 3) were used to characterize the flow behavior of the starch paste. The power law parameters K and n were computed from linear regression analysis of $\log \tau$ versus $\log \dot{\gamma}$. The Herschel-Bulkley model was studied in two ways. One was to determine parameters K and n

with a given yield stress, i.e., the magnitude of yield stress obtained from direct measurement was subtracted from those of shear stress and the magnitudes of K and n were then determined from linear regression analysis of $\log (\tau - \tau_y)$ versus $\log \dot{\gamma}$. The other was to use non-linear regression analysis to compute the yield stress (τ_o), K, and n.

The Casson model (Equation 21) has been employed to determine the yield stress of chocolate (Rao, 1977) and to characterize the flow behavior in some fluid foods (Charm, 1963b; Duran and Costell, 1982):

$$\tau^{0.5} = K_o + K_c \cdot \dot{\gamma}^{0.5} \qquad (21)$$

Its applicability to the flow data of starch pastes was also studied using linear regression analysis of $\log \tau^{0.5}$ versus $\log \dot{\gamma}^{0.5}$ to determine K_o and K_c. K_c is the consistency index and K_o^2 is known to be the Casson yield stress.

Each set of the flow curve data (12 points in each curve) was used in the above mentioned flow models for regression analysis.

Statistical Analysis

The "Statistical Package for the Social Sciences" computer programs described by Nie et al. (1975) for use on the CDC 6500 computer laboratory was used to assist statistical analysis.

Multivariate analysis of variance was used to determine the effect of treatments with subprogram ANOVA. Single classification analysis of variance and Tukey mean separations were determined with subprogram ONEWAY.

The treatment means with like letters in Tukey mean separation indicated no significant differences at $P < 0.05$. Mean squares with

significant F ratios were reported with probability levels of $P < 0.05$ (*), $P < 0.01$ (**), and $P < 0.001$ (***). Coefficient of Variation (CV) which expresses the standard deviation as a percent of the mean was calculated (Little and Hills, 1972).

Linear and non-linear regression analyses were employed for flow curve data using subprograms REGRESSION and NONLINEAR (Nie et al., 1975). The square of correlation coefficients, r^2, for linear regression and the sum-of-squares function, SS(b), for non-linear regression were reported to indicate the goodness of curve fitting.

RESULTS AND DISCUSSION

Study 1: Physicochemical Characteristics of Dry-Roasted Navy Bean Flour Fractions

Chemical Composition

Table 1 shows the yields of the fractionation process and chemical composition of dry-roasted navy bean flour fractions. After roasting and dehulling whole navy beans, 10% hull flour and 90% cotyledons were obtained. Grinding and air-classification of the cotyledons then yielded 32% of high protein flour and 55% high starch flour. The yields of high protein and high starch flour are similar to those reported by Patel et al. (1980) and Sahasrabudhe et al. (1981). Protein content of high protein flour, however, was 41.31%. This was lower than that claimed by Sahasrabudhe et al. (1981) who used air-classification technique on four white bean cultivars to obtain 50% to 56% protein in high protein flour. Patel et al. (1980) reported 61.9% in air-fractionated protein concentrate from whole bean flour having a higher initial protein content. High starch flour obtained from this study contained 16.12% protein which is 6% to 8% higher than that obtained by the aforementioned researchers. Starch content in high starch flour was demonstrated to be significantly higher than that in whole flour and high protein flour (Table 1). High starch flour showed a similar starch value to that reported by Tyler et al. (1981). However, high

Table 1. Yield and chemical analyses of dry-roasted navy bean flour fractions[1]

Flour Fraction	Yield (%)	Moisture (% wb)	Fat (% db)	Protein (% db)	Ash (% db)	ENDF[2] (% db)	Starch (% db)	NSI[3]
Whole	100	8.92 ± 0.04c	1.82 ± 0.12b	25.94 ± 0.38c	5.25 ± 0.72c	7.58 ± 0.12c	60.46 ± 2.24b	39.77 ± 0.58b
Hull	10	9.03 ± 0.03c	1.01 ± 0.15a	18.44 ± 0.77b	6.32 ± 0.45c	35.43 ± 0.10d	---	27.49 ± 1.16a
High Protein	32	7.05 ± 0.12a	2.49 ± 0.22c	41.31 ± 0.32d	4.72 ± 0.05b	4.45 ± 0.08b	31.94 ± 4.72a	43.29 ± 0.32c
High Starch	55	8.35 ± 0.07b	1.02 ± 0.13a	16.12 ± 0.29a	2.69 ± 0.08a	2.30 ± 0.08a	67.72 ± 2.05c	45.36 ± 0.81d

[1]Mean values and standard deviations (like letters within each column indicate no significant differences at $P < 0.05$ by Tukey mean separation; $n = 3$)

[2]Enzyme neutral detergent fiber (Robertson and Van Soest, 1977)

[3]Nitrogen solubility index

protein flour contained a much higher starch value than that reported by Tyler et al. (1981).

Four flour fractions were assessed for oligosaccharides by HPLC to determine potential problems with flatulence developed after ingestion (Wagner et al., 1977). HPLC sugar analysis of the flour fractions showed that stachyose was the major oligosaccharide, followed by sucrose and glucose with trace amounts of raffinose in all fractions (Figure 12). Hull flour contained the lowest total sugar among fractions. High protein flour had similar amounts of glucose, sucrose, and raffinose as whole bean flour, but significantly higher stachyose levels. High starch flour contained about the same amount of sugars as whole bean flour except that the sucrose level was significantly lower. Stachyose contents detected in whole bean flour, hull flour, and high protein flour were generally lower than those reported by Sahasrabudhe et al. (1981).

Physical Functionality

HunterLab color values (Table 2) indicated that hull flour was appreciably darker, more red, and more yellow than the other fractions. On the other hand, high protein flour showed the lightest, most green, and least yellow color among fractions.

Three bean flour fractions were substituted for 10% bread flour to study rheological properties of the dough and the results are presented in Table 3. Farinograms showed changes in arrival time and a slight, but consistent, decrease in peak time for all fractions. Water absorption and dough stability were greatly affected. Substituting 10% bean hull flour had the greatest effect in increasing water absorption. The 60.8% water absorption value for wheat flour standard

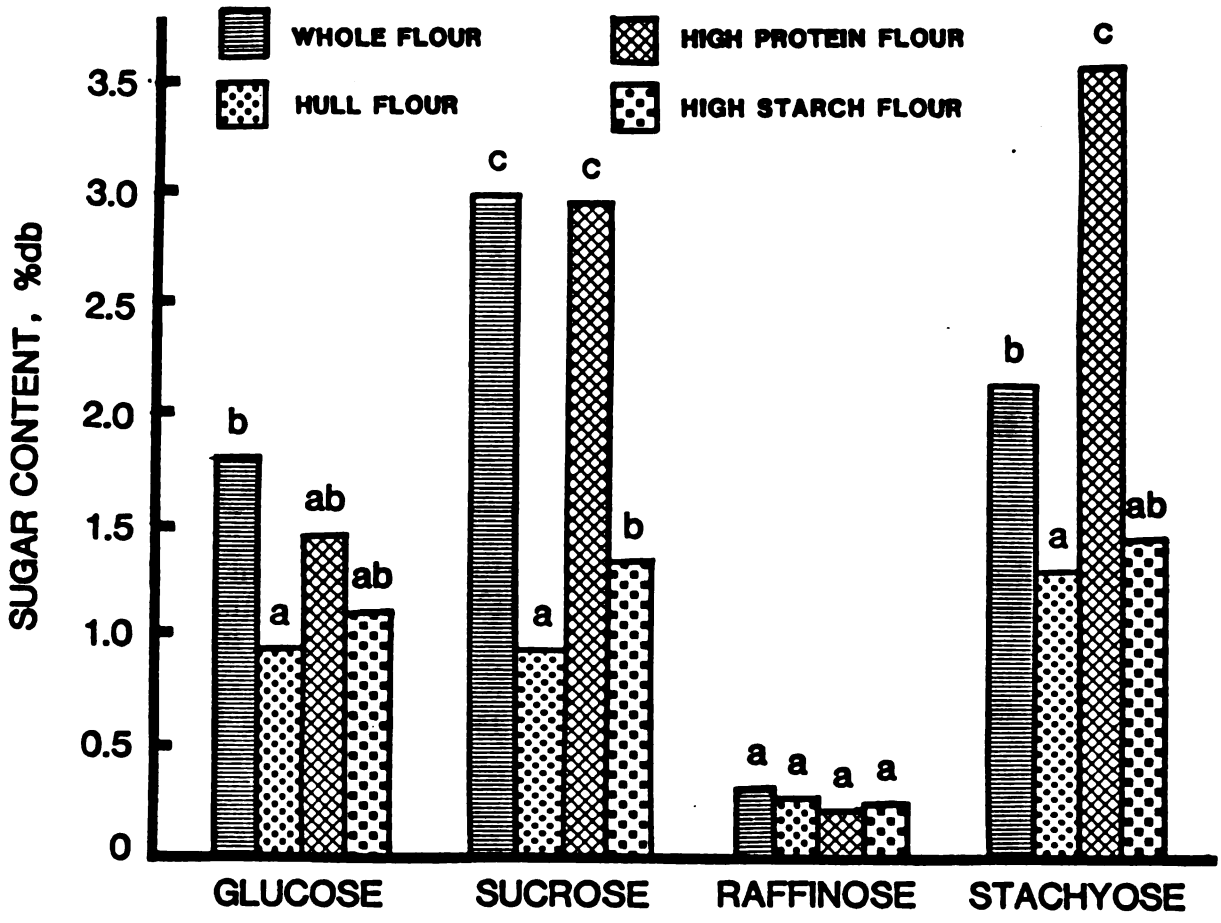


Figure 12. HPLC sugar analysis of dry-roasted navy bean flour fractions (like letters within each group indicate no significant differences at $P<0.05$ by Tukey mean separation)

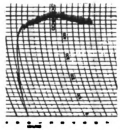
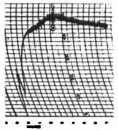
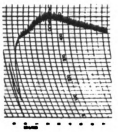
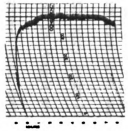
Table 2. HunterLab color values of dry-roasted navy bean flour fractions[1]

Flour Fraction	HunterLab Color Values[2]		
	L	a_L	b_L
Whole	85.10±0.10b	-2.37±0.06b	9.77±0.06b
Hull	77.13±0.06a	-2.03±0.06c	11.87±0.06d
High Protein	87.43±0.06d	-2.57±0.06a	8.13±0.06a
High Starch	85.67±0.06c	-2.47±0.06ab	10.23±0.06c

[1]Mean values and standard deviations (like letters within each column indicate no significant differences at $P < 0.05$ by Tukey mean separation; $n = 3$)

[2]Standardized to a white tile: $L = 95.35$, $a_L = -0.6$, $b_L = +0.4$

Table 3. Farinograph values of dry-roasted navy bean flour fractions[1,2]

Paramater	Flour Fractions			
	Whole Flour	Hull Flour	High Protein Flour	Wheat Flour Standard
Curve Type				
Water Absorption (%)	61.3±0.5 a	74.4±0.1 c	71.1±0.1 b	60.8±0.2 a
Arrival Time (min.)	3.0±0.1 a	3.5±0.0 c	3.2±0.0 b	3.0±0.1 a
Peak Time (min.)	4.3±0.1 a	4.4±0.1 a	4.3±0.1 a	5.0±0.1 b
Stability (min.)	3.5±0.1 c	2.3±0.3 a	3.0±0.1 b	6.0±0.2 d

[1]Mean values and standard deviations (like letters within each row indicate no significant differences at $P < 0.05$ by Tukey mean separation; $n = 3$)

[2]Bean fractions substituted 10% for wheat flour

increased to 74.4% while the mixing stability changed from 6.0 min to 2.3 min. Whole bean flour had the least effect with a water absorption of 61.3% and a dough stability of 3.5 min. The effect of substituting the high protein fraction was slightly less detrimental than that which occurred with navy bean hulls. The increase in water absorption and reduction in dough stability due to the substitution of bean flour generally agreed with data reported by D'Appolonia (1978) and Sathe et al. (1981b).

Pasting curves of whole bean and high starch flours and corn starch as comparison are shown in Figure 13. The viscoamylograph indicated that the whole bean flour produced a viscous suspension with controlled swelling. Maximum gelatinization of 550 Brabender Units (B.U.) was not reached until the ambient hot (95°C) stirring portion of the curve. This was approximatley 100 B.U. more than the viscosity during the heating portion of the curve. Upon cooling, the viscosity showed a moderate increase indicating a tendency toward association of starch molecules. Gelatinization of the high starch fraction gave a similar viscoamylograph curve; however, maximum gelatinization occurred at 630 B.U. Naivikul and D'Appolonia (1979) reported that navy bean starch isolate had a peak height at 530 B.U. which was 100 B.U. lower than that reported in this study. The curves in Figure 13 show that whole flour and its high starch flour fractions have higher resistance to swelling than does corn starch. Slurries of two flour fractions were stable during heating and stirring; however, the slurry of corn starch showed disintegration of granules.

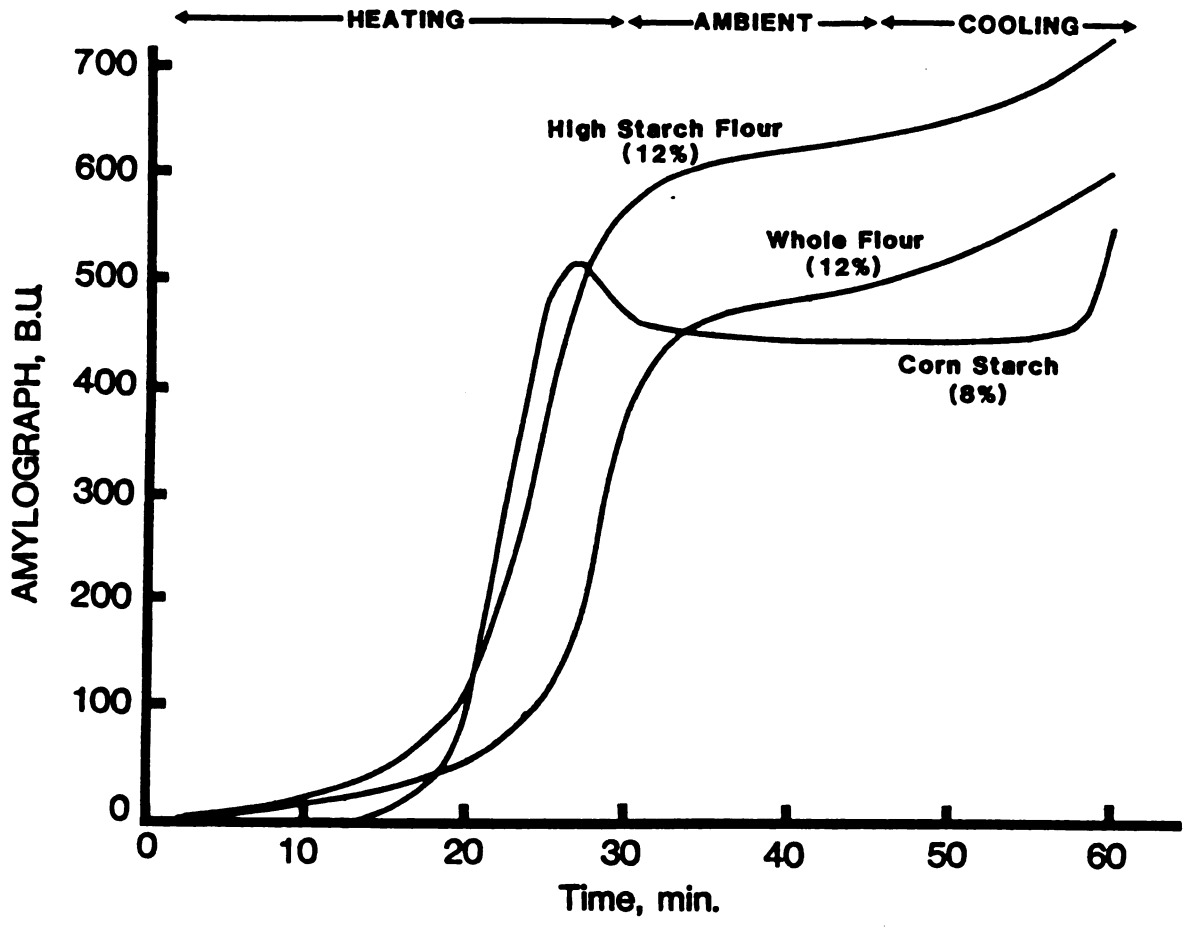


Figure 13. Pasting characteristics of dry-roasted navy bean whole and high starch flour fractions and a corn starch

Study 2: Effect of Roasting and Storage Conditions on the Stability of Air-Classified Navy Bean Flour Fractions

Proximate Composition of Flour Fractions

Proximate composition of the air-classified flour fractions obtained from beans after various roasting treatments is shown in Table 4.

Equilibrium Moisture Content

The effect of roasting conditions on the equilibrium moisture content (EMC) of the air-classified navy bean flour fractions in various water activity (a_w) levels was determined at room temperature. Figure 14 illustrates the water asorption isotherms of whole flours for different roasting treatments in various a_w levels after eight weeks of storage. Roasting treatment did not affect the equilibrium moisture content of the flours to a significant extent for the two lowest a_w levels (0.48 and 0.53); however, EMC of whole flours decreased with increased roasting time and temperature and the effect of time/temperature treatment was shown to be significant with increased a_w, especially with a_w's beyond 0.8.

A similar roasting effect was shown for the water asorption isotherms of hull flours except that the most severe roasting did not affect the EMC as dramatically as it did whole flours for the highest a_w (Figure 15).

The water asorption isotherms of high protein flours are shown in Figure 16. Roasting did not affect EMC of these flours significantly for the lowest a_w level (0.48) and similar isotherms were obtained for

Table 4. Proximate composition of dry-roasted navy bean flour fractions obtained from beans processed at various conditions[1]

Treatment Time, Temp (min, °C)		Moisture (% wb)	Fat (% db)	Protein (% db)	Ash (% db)	ENDF[2] (% db)	NSI[3]
Whole Flour							
1	240	8.92	1.82	25.94	5.25	7.58	39.77
	270	8.45	2.00	25.88	4.45	7.50	35.02
2	240	8.03	2.09	25.38	4.82	6.89	20.69
	270	8.02	1.91	25.50	4.06	8.61	16.67
Hull Flour							
1	240	9.03	1.01	18.44	6.32	35.43	27.49
	270	8.06	0.49	15.31	6.25	40.18	26.94
2	240	8.55	1.31	17.81	5.79	31.24	25.96
	270	7.12	1.94	14.13	6.35	40.43	23.89
High Protein Flour							
1	240	7.05	2.49	41.31	4.72	4.45	43.29
	270	6.92	2.70	42.56	4.88	3.74	30.84
2	240	6.48	3.23	47.63	5.11	4.29	28.35
	270	6.08	2.67	39.25	4.49	3.38	17.04
High Starch Flour							
1	240	8.35	1.02	16.12	2.69	2.30	45.36
	270	7.99	1.08	15.50	3.14	3.32	32.66
2	240	7.10	0.88	12.94	3.03	2.49	31.40
	270	6.52	0.91	13.81	3.12	2.65	27.15

[1] $n = 3$

[2] Enzyme neutral detergent fiber (Robertson and Van Soest, 1977)

[3] Nitrogen solubility index

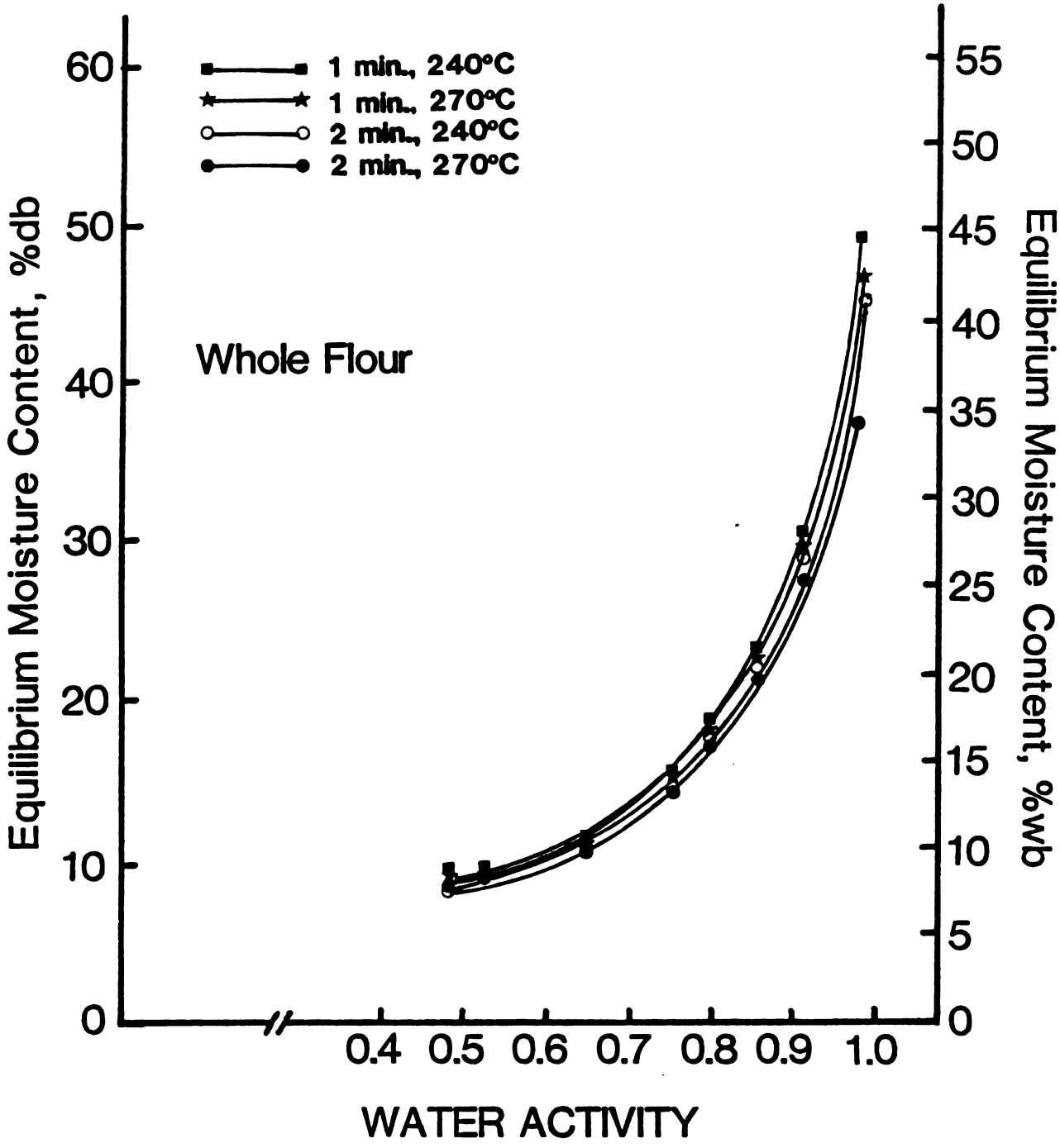


Figure 14. Water asorption isotherms of dry-roasted navy bean whole flours at room temperature (20°C)

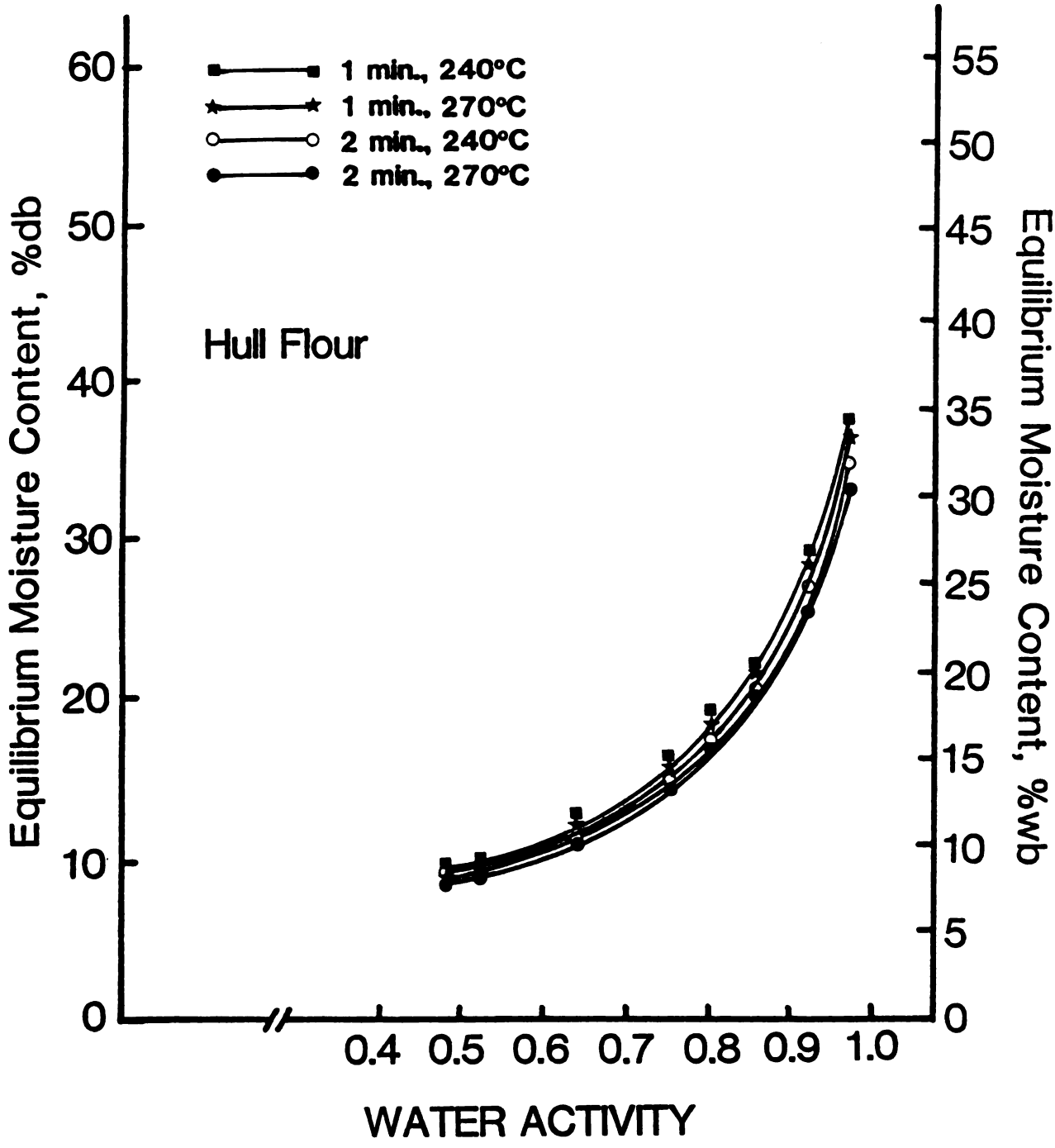


Figure 15. Water asorption isotherms of dry-roasted navy bean hull flours at room temperature (20°C)

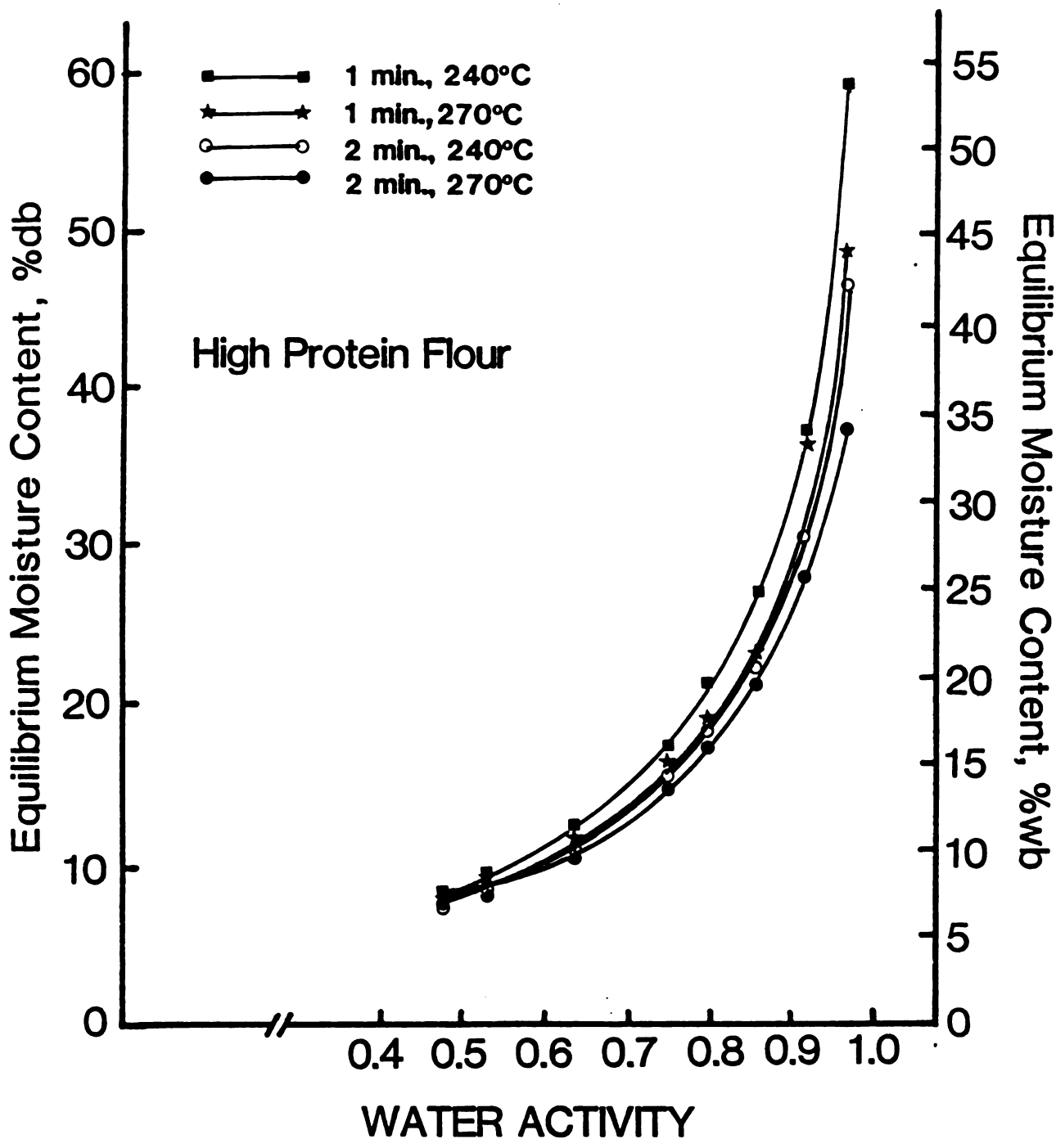


Figure 16. Water asorption isoterms of dry-roasted navy bean high protein flours at room temperature (20°C)

flours from roasting treatments of 1 min/270°C and 2 min/240°C. In general, EMC of high protein flours decreased significantly with increased roasting time and temperature over the range of a_w in which flours were stored.

Isotherm curves of high starch flours as affected by roasting were similar to those for whole flours except that slightly lower EMC values were found for high starch flours at higher a_w levels (Figure 17).

Comparisons of isotherms from these figures demonstrated that high protein flours having the highest protein content (41.3% to 47.6% db) had the highest EMC among all fractions, while hull flour with somewhat lower protein content (14.1% to 18.4%) had the lowest EMC at all a_w levels. To compare the capability of water uptake among fractions, the isotherms obtained from roasting treatment of 1 min at 240°C are presented in Figure 18. EMC of high protein flour was the highest among all fractions while that of hull flour was the lowest at all a_w levels.

Surface Mold Growth

Mold growth on the surface of flour samples was observed during the storage period. Flours stored in a_w's less than 0.75 did not show mold growth throughout the storage period; however, mold mycelia were observed on the flours held under 0.92 and 0.97 a_w after one week. Since the effect of roasting on mold growth was not evident, data were pooled from all four roasting treatments for each flour fraction to assess the influence of moisture content on mold growth of the flour fractions during storage (Figure 19). Generally, moisture content of samples beyond 16% db caused significant increases of mold growth for all the flour fractions. High protein flour had the highest water

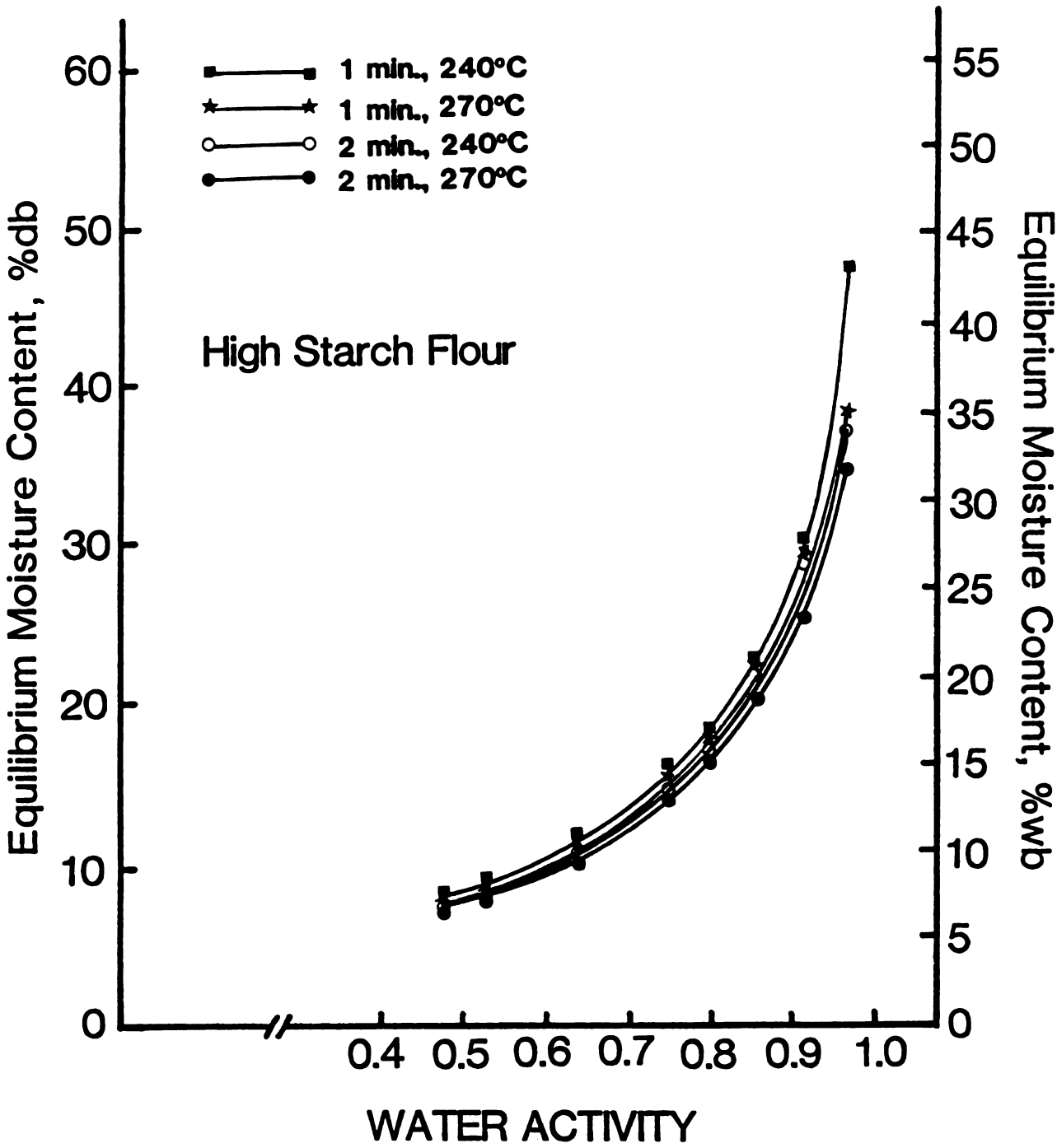


Figure 17. Water asorption isotherms of dry-roasted navy bean high starch flours at room temperature (20°C)

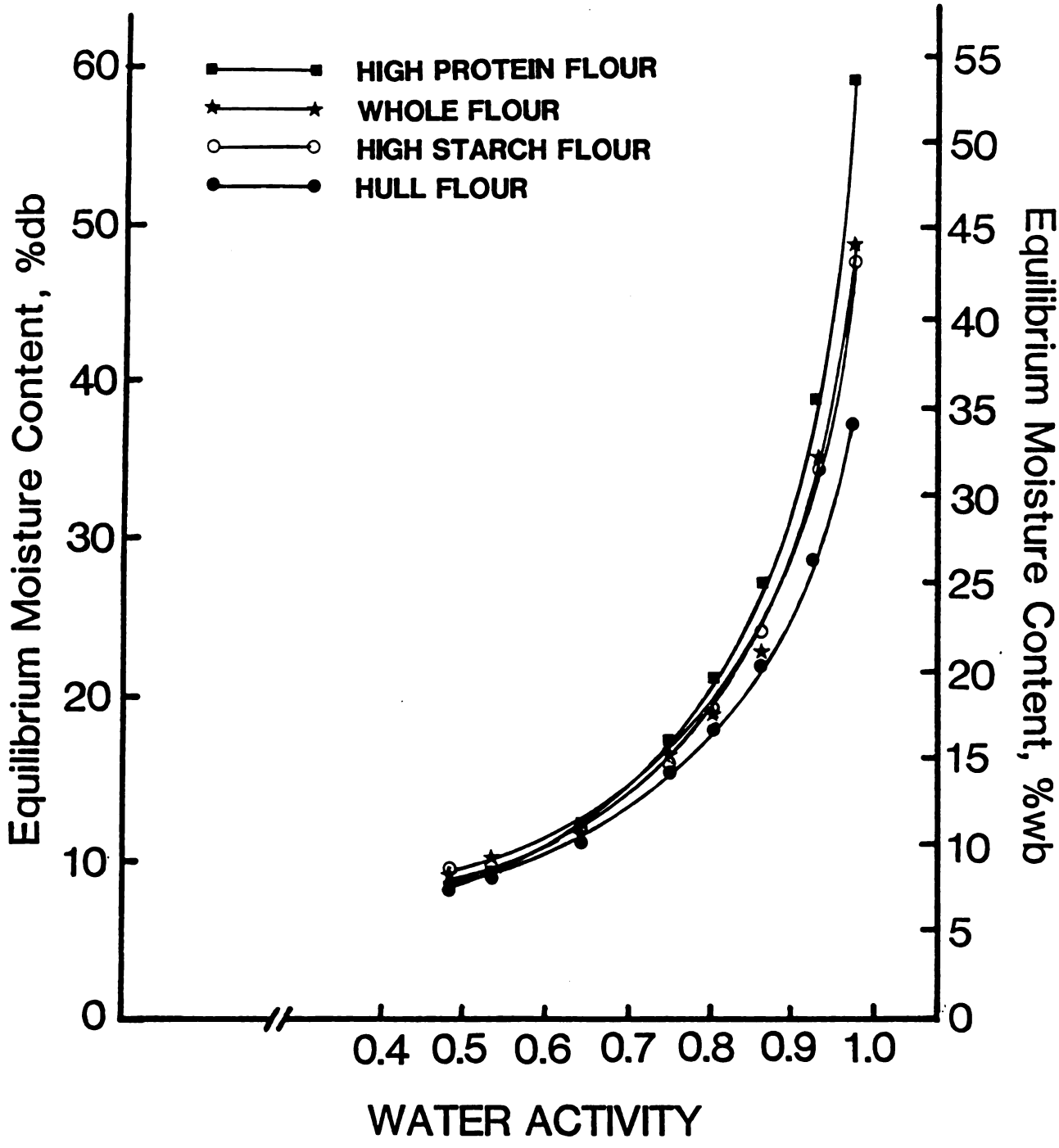


Figure 18. Water asorption isotherms of dry-roasted navy bean flour fractions obtained from beans processed at 240°C for 1 min

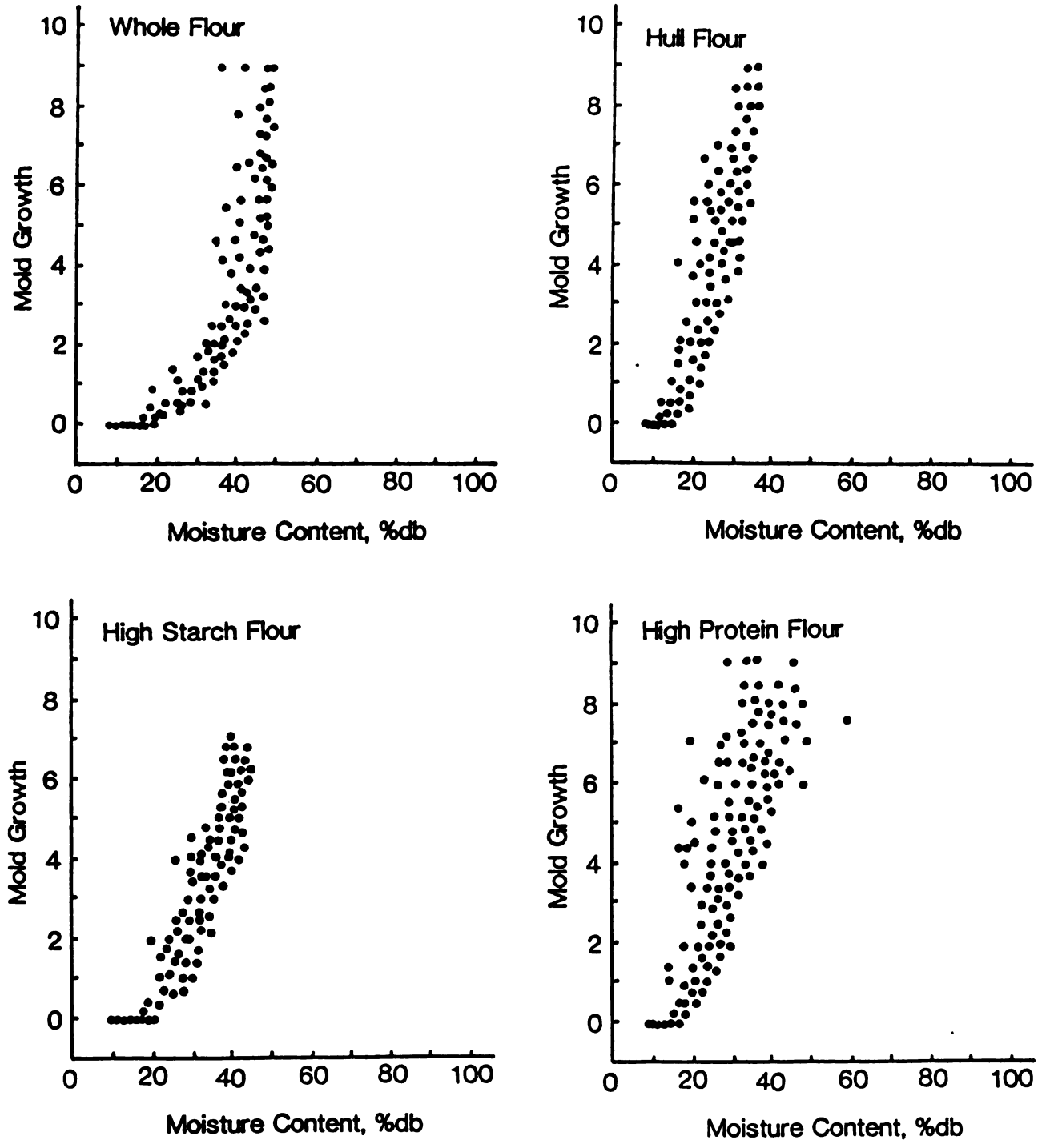


Figure 19. Mold growth of dry-roasted navy bean flour fractions at various moisture contents during storage

uptake and thus resulted in the most mold growth, whereas the high starch flour absorbed the least water and had the least mold growth. EMC of the hull flour after eight weeks was lower than 40% db; however, there was considerable mold growth on the flour surface. This may have been due to the contamination of molds on the seedcoats of beans prior to roasting.

Property Changes after Storage

Following storage the samples in a_w higher than 0.75 were moldy and thus discarded. Since the roasting treatment of 1 min at 240°C was demonstrated to obtain the highest EMC after storage, flours from this treatment were selected for color, NSI, and sugar analyses.

Mean HunterLab color values and Tukey mean separations for flour fractions stored in 0.48, 0.53,0.64, and 0.75 a_w for eight weeks are presented in Table 5. Hunter L values remained unchanged with increased a_w for all the flour fractions; however, a_L and b_L values of these fractions increased with increased a_w indicating that flours became more red and more yellow toward higher a_w levels.

Labuza et al. (1970) stated that non-enzymatic browning increased with increased a_w reaching a maximum and then decreased due to the dilution of the reactants. The fact that discoloration of flours increased with increased a_w in this study could be due to the increased browning reactions in the stored samples at higher a_w levels.

Nitrogen solubility indices (NSI) were evaluated for flours stored in increased a_w as shown in Figure 20. NSI values were found to decrease significantly for whole flours and high starch flours stored beyond 0.48 a_w and for high protein flour stored beyond 0.53 a_w. In general, NSI values of these fractions decreased with increased storage a_w except for hull flour. NSI values of hull flours were the lowest

Table 5. HunterLab color values of dry-roasted navy bean flour fractions stored under various water activity levels for eight weeks[1]

Water Activity	HunterLab Color Values[2]		
	L	a_L	b_L
Whole Flour			
Initial	85.1a	-2.4a	9.8a
0.48	84.3a	-1.7ab	11.4b
0.53	84.8a	-2.1a	10.0ab
0.64	84.8a	-1.4b	11.6b
0.75	84.1a	-0.2c	13.8c
Hull Flour			
Initial	77.1a	-2.0a	11.9a
0.48	76.8a	-1.7a	12.3a
0.53	77.1a	-1.8a	11.8a
0.64	76.8a	-1.0b	14.2b
0.75	76.3a	-0.3c	15.6b
High Protein Flour			
Initial	87.4a	-2.6a	8.1a
0.48	86.9a	-1.8ab	9.6a
0.53	86.9a	-2.4a	7.8a
0.64	87.4a	-2.2a	8.7a
0.75	86.5a	-0.7c	11.8b
High Starch Flour			
Initial	85.7a	-2.5a	10.2a
0.48	85.3a	-1.9ab	11.7a
0.53	85.7a	-2.3a	10.4a
0.64	85.6a	-1.6b	11.0a
0.75	84.2a	-0.2c	13.9b

[1]Mean values (like letters within each column for each flour fraction indicate no significant differences at $P<0.05$ by Tukey mean separation; $n = 3$)

[2]Standardized to a white tile: $L = 95.35$, $a_L = -0.6$, $b_L = 0.4$

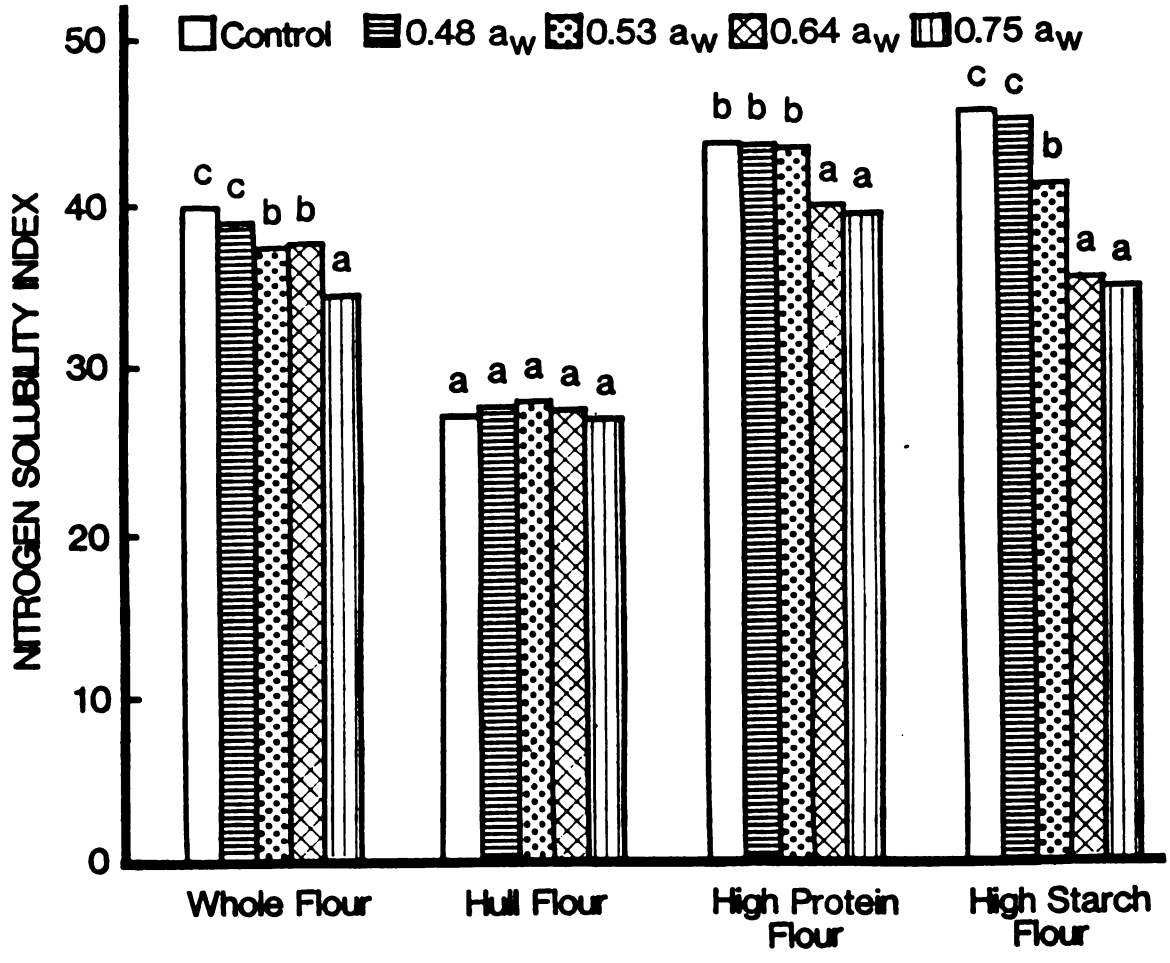


Figure 20. Nitrogen solubility indices of dry-roasted navy bean flour fractions stored under various water activity levels for eight weeks

among fractions and did not show any significant change due to increased a_w levels.

Sugar contents of flours were analyzed by HPLC using a carbohydrate analysis column. Mean values of the sugars and Tukey mean separations for flour fractions stored in various a_w's are shown in Table 6. In general, glucose decreased significantly, with increased a_w for all the fractions. Other sugars remained unchanged or decreased with increasing a_w. The reduction of glucose was probably attributed to the increased non-enzymatic browning reactions which also cause the increased discoloration of flours at higher a_w levels.

Lea and White (1948) found that dry skim milk with high moisture content discolored most and showed the greatest insolubility due to the reaction of amino acid with the reducing sugar in the product. They concluded that a_w in the powder determined the rate of deterioration. The present study agrees with their findings in that increased browning reactions occurred at higher a_w's with concurrent decrease of the protein solubility and glucose levels.

Starch content was analyzed for flours after storage using the YSI Industrial Analyzer and the mean values and Tukey mean separations are presented in Table 7. Data indicated that significant change of the starch content only occurred at 0.75 a_w for fractions except for hull flour where the change occurred at lower water activity. The reduction of starch content at high water activity could be due to the hydrolysis of starch molecules into glucose units, which were washed off during extraction procedures, leading to low readings in starch analysis.

Table 6. HPLC sugar analysis of dry-roasted navy bean flour fractions stored under various water activity levels for eight weeks[1]

Water Activity	Glucose	Sucrose	Raffinose	Stachyose
	(% db)			
Whole Flour				
Initial	1.79c	3.00a	0.32a	2.14bc
0.48	1.25b	2.35a	0.38a	2.25c
0.53	1.21ab	2.40a	0.24a	2.23c
0.64	1.30b	2.58a	0.32a	1.80a
0.75	1.10a	2.62a	0.28a	1.91ab
Hull Flour				
Initial	0.91c	0.92b	0.29a	1.34a
0.48	0.71b	1.00c	0.28a	1.36a
0.53	0.68b	0.95bc	0.27a	1.33a
0.64	0.46a	0.91b	0.26a	1.38a
0.75	0.50a	0.87a	0.29a	1.32a
High Protein Flour				
Initial	1.47c	2.95c	0.24b	3.60c
0.48	1.34b	3.00c	0.29c	3.73c
0.53	1.35b	2.32ab	0.28c	3.27b
0.64	1.14a	2.52b	0.20ab	3.10a
0.75	1.20a	2.07a	0.17a	3.12a
High Starch Flour				
Initial	1.10c	1.36a	0.25b	1.44b
0.48	0.89b	1.39a	0.26b	1.49b
0.53	0.81b	1.34a	0.22b	1.45b
0.64	0.93b	1.38a	0.19ab	1.43b
0.75	0.72a	1.36a	0.17a	1.23a

[1]Mean values (like letters within each column for each flour fraction indicate no significant differences at $P < 0.05$ by Tukey mean separation; $n = 3$)

Table 7. Starch analysis of dry-roasted navy bean flour fractions stored under various water activity levels for eight weeks[1]

Flour Fraction	Water Activity				
	Initial	0.48	0.53	0.64	0.75
Whole	60.46b	59.00b	57.19b	57.48b	47.16a
Hull	31.85c	29.68c	29.77c	28.35b	27.20a
High Protein	31.94b	31.04b	31.54b	30.96b	29.56a
High Starch	67.72b	67.54b	67.32b	66.95b	64.30a

[1]Mean values (like letters within each row indicate no significant differences at $P<0.05$ by Tukey mean separation; n =3)

Long Term Storage Stability

In order to further evaluate the stability of flours during long term storage, flour fractions from the optimum roasting treatment were selected and stored at two temperatures and three preadjusted moisture contents for up to 24 months.

Table 8 shows the mean color values and Tukey mean separations for these flour fractions. In general, the Hunter L, a_L, and b_L values did not change significantly for flours stored at 20°C with moisture content up to 9% and at 37.7°C with moisture content of 6%. Extended storage time from 12 months to 24 months did not have adverse effects on flour color at the above conditions.

Nitrogen solubility and lipid oxidation of the flours were evaluated after 12 and 24 months. Mean NSI and 2-thiobarbituric acid (TBA) values and Tukey mean separations are presented in Table 9.

Table 8. HunterLab color values of dry-roasted navy bean flour fractions stored at varying moisture contents at 20°C and 37.7°C for up to 24 months[1]

Treatment Temp, Moisture (°C, % db)		HunterLab Color Values[2]					
		L		a_L		b_L	
		12 mo.	24 mo.	12 mo.	24 mo.	12 mo.	24 mo.
Whole Flour							
20	6	85.1b	85.2c	-2.4a	-2.4a	9.8a	9.9a
	9	85.1b	85.1c	-2.1a	-2.0b	10.2a	10.4ab
	12	84.9b	84.5bc	-1.8b	-1.8ab	11.5c	12.0c
37.7	6	85.0b	84.8c	-2.2a	-2.2a	10.0a	10.1a
	9	84.6b	83.5b	-1.8b	-1.5c	10.7b	11.0b
	12	83.2a	82.1a	-1.5c	-1.2c	12.8d	13.9d
Hull Flour							
20	6	77.0b	76.8c	-2.0b	-1.9b	12.3a	12.2a
	9	77.3b	76.8c	-1.9b	-1.7b	12.1a	12.2a
	12	77.2b	76.5c	-1.6a	-1.6b	13.8b	13.9bc
37.7	6	77.2b	76.8c	-2.0b	-1.5ab	12.5a	13.1c
	9	77.0b	75.2b	-1.5a	-1.2a	13.4b	14.2c
	12	74.4a	74.0a	-1.4a	-1.0a	14.2c	15.8d
High Protein Flour							
20	6	87.5b	87.4b	-2.6c	-2.6b	8.1a	8.0a
	9	87.8b	87.5b	-2.5c	-2.4b	8.1a	8.2a
	12	87.6b	87.6b	-2.4c	-2.4b	8.0a	8.2a
37.7	6	87.6b	87.2b	-2.4c	-2.2b	8.0a	8.4b
	9	87.2b	87.5b	-2.0b	-1.9ab	8.4b	8.7bc
	12	85.9a	84.3a	-1.6a	-1.4a	8.9c	9.2c
20	6	85.6a	85.5a	-2.5a	-2.5a	10.3a	10.3a
	9	85.7a	85.4a	-2.2ab	-2.3ab	10.6a	10.6a
	12	85.4a	85.2a	-2.0b	-2.0b	10.6a	10.8ab
37.7	6	85.7a	85.0a	-2.2ab	-2.0b	10.4a	10.5a
	9	85.2a	85.1a	-2.0b	-1.8bc	11.1b	11.5b
	12	84.8a	84.9a	-1.8c	-1.6c	11.2b	12.0b

[1]Mean values (like letters within each column for each flour fraction indicate no significant differences at $P < 0.05$ by Tukey mean separation; $n = 3$)

[2]Standardized to a white tile: $L = 95.35$, $a_L = -0.6$, $b_L = 0.4$

Table 9. Nitrogen solubility indices and TBA values of dry-roasted navy bean flour fractions stored at varying moisture contents at 20°C and 37.7°C for up to 24 months[1]

Treatment Temp, Moisture (°C, % db)		NSI		TBA	
		12 mo.	24 mo.	12 mo.	24 mo.
Whole Flour					
20	6	39.76c	39.82c	0.52a	0.50a
	9	39.05c	39.99c	0.61ab	0.64b
	12	37.25b	36.90b	0.70b	0.75b
37.7	6	38.20bc	35.29b	1.02c	1.32c
	9	34.96a	32.38a	1.35d	1.89d
	12	34.20a	33.65a	1.41d	1.95d
Hull Flour					
20	6	27.50b	26.80b	0.45a	0.44a
	9	27.25b	26.52b	0.45a	0.47a
	12	27.38b	26.75b	0.44a	0.47a
37.7	6	27.10b	26.25b	0.47a	0.43a
	9	26.90b	26.51b	0.45a	0.45a
	12	22.98a	23.05a	0.48a	0.43a
High Protein Flour					
20	6	43.25c	43.00c	0.82a	0.82a
	9	42.33c	43.25c	0.85a	0.83a
	12	40.62bc	39.32bc	0.81a	0.82a
37.7	6	43.20c	40.25c	1.68b	1.65b
	9	37.52ab	34.84ab	1.80b	1.86c
	12	34.35a	31.65a	1.78b	1.95c
High Starch Flour					
20	6	45.38b	44.63c	0.64a	0.65a
	9	44.25b	44.32c	0.68a	0.69a
	12	44.10b	44.62c	0.69a	0.65a
37.7	6	43.65b	40.24b	0.66a	0.66a
	9	38.75a	36.25a	0.65a	0.66a
	12	39.25a	35.15a	0.69a	0.69a

[1]Mean values (like letters within each column for each flour fraction indicate no significant differences at $P < 0.05$ by Tukey mean separation; $n = 3$)

Significant adverse effects occurred only to the flours stored at 37.7°C with moisture contents of 9% and 12% after 12 and 24 months.

TBA values were determined for the flours to examine the oxidation of fatty acids (Table 9). TBA values greater than 1 will generally be detected by the consumers or taste panelists and, therefore, the value of 1 was used as a cutoff point. Whole and high protein flours stored at 20°C with three moisture levels for up to 24 months were considered acceptable. After storage of these two flour fractions at 37.7°C, however, TBA values indicated detectable rancidity for all moisture contents after 12 and 24 months. There was no significant adverse effect on TBA values for either hull flour or high starch flour under any condition. This could be due to the low fat content (about 1%) in these flours.

Study 3: Gelatinization and Rheological Properties of Purified Navy Bean Starch Pastes

Proximate Composition of Purified Starch

Purification of the air-classified high starch flour resulted in a significant increase in starch content. Table 10 shows the proximate composition of the air-classified high starch flour and purified starch.

Preparation of Starch Paste

Starch granules will swell in the presence of water with sufficient heat supply. To a certain extent, the swollen granules are highly susceptible to thermal and mechanical breakdown due to their swollen and fragile conditions and increasing weakening of bonding forces within the micellar network. The system is govered by two processes which affect the viscosity in opposite ways at this stage of cooking. One

Table 10. Proximate composition of air-classified high starch flour and purified starch of navy beans[1]

Starch	Moisture (% wb)	Fat (% db)	Protein (% db)	Ash (% db)	ENDF (% db)	Starch (% db)
Air-Classified	9.79	1.47	15.51	3.63	1.76	65.43
Purified	7.22	0.11	0.98	0.46	0.51	91.17

[1] n = 3

process is the continuous swelling of the granules which increases the viscosity; the other process is the disintegration of the already swollen granules which causes viscosity decrease. Prolonged heating of the paste will cause breakdown of the granules and, consequently, leads to the reduction of viscosity. Rheological measurement of the paste made at this cooking stage, which exhibits a continuous structural change, may result in unreliable information for its flow behavior.

This study emphasized the preparation and gelatinization of starch pastes under specified conditions. The torque response due to swelling and/or breakdown of starch granules during cooking was monitored. The curves generated from these torque responses for various treatments were termed "thermal response curves."

The perforated paddle mixer was chosen to prepare starch pastes in an MV1 cup prior to rheological measurements with an MV1 bob. Preliminary experimentation was conducted to measure the torque values of pastes during cooking at selected temperatures and stirring at a range of paddle rotation speeds. Results indicated that 50 rpm was the optimum speed for

minimum mechanical breakdown of the pastes and yet provided homogeneous starch suspensions without starch precipitation at the lowest temperature (75°C) tested.

In general, two types of the thermal response curves were found in this test: one being a gradual increase of the torque value which approached an equilibrium torque value and the other being a relatively rapid increase of the torque value to a peak followed by a decline before reaching an equilibrium torque.

Preliminary experimentation indicated that paddle speeds lower than 25 rpm resulted in precipitation of granules for 6%, 8%, and 10% starch suspensions when cooked at 75°C. On the other hand, the speeds higher than 75 rpm caused dramatic breakdown of the paste bodies at high temperatures and concentrations and, therefore, were not desirable for monitoring the gelatinization process. The three speeds, 25 rpm, 50 rpm, and 75 rpm, were then chosen for comparisons. Table 11 represented final torque values after 60 min shearing at paddle speeds of 25 rpm, 50 rpm, and 75 rpm for 10% starch paste cooked at 75°C and 95°C. At the end of shearing at a particular speed, the paddle was switched to two other speeds to obtain two torque responses. Results indicated that pastes stirred at 50 rpm had the highest torque values.

Heating rate of the starch has been reported to affect the final viscosity of starch paste. Therefore, the rapid heating process as employed in this study was compared with the slow heating which is commonly used in the preparation of starch pastes. Figure 21 shows the thermal response curves for 10% starch paste cooked at 75°C and 95°C with rapid heating (about 5 min to reach cooking temperature) and slow heating (1.5°C/min). For each condition, the difference of the final

torque values demonstrated to be insignificant between the two heating processes.

Table 11. Final torque values for 10% navy bean starch pastes stirred at various paddle speeds and cooked at 75°C and 95°C for 60 min[1]

Paddle Rotation Speed (rpm)	Torque (N-m x 10^{-2})					
	75°C			95°C		
	25	50	75	25	50	75
	test speed (rpm)					
25	0.095	0.112	0.120	0.440	0.482	0.510
50	0.124	0.140	0.152	0.495	0.520	0.540
75	0.110	0.126	0.132	0.420	0.480	0.534

[1] n = 3

Starch Gelatinization

The torque values, indicating the resistance of the paste flow to the paddle, were recorded continuously through the HP 85 during cooking. While the well-mixed starch suspensions were stirred with a paddle mixer in the MV cup, starch granules swelled or gelatinized to give increased flow resistance, thereby increasing torque values. A more viscous starch paste was expected to give a higher torque value while a less viscous paste was expected to give a lower torque value. Increased torque value therefore indicated an increase in paste viscosity.

Figure 22 illustrates the response curves of 6% starch pastes under various cooking temperatures. The dotted vertical line indicates the

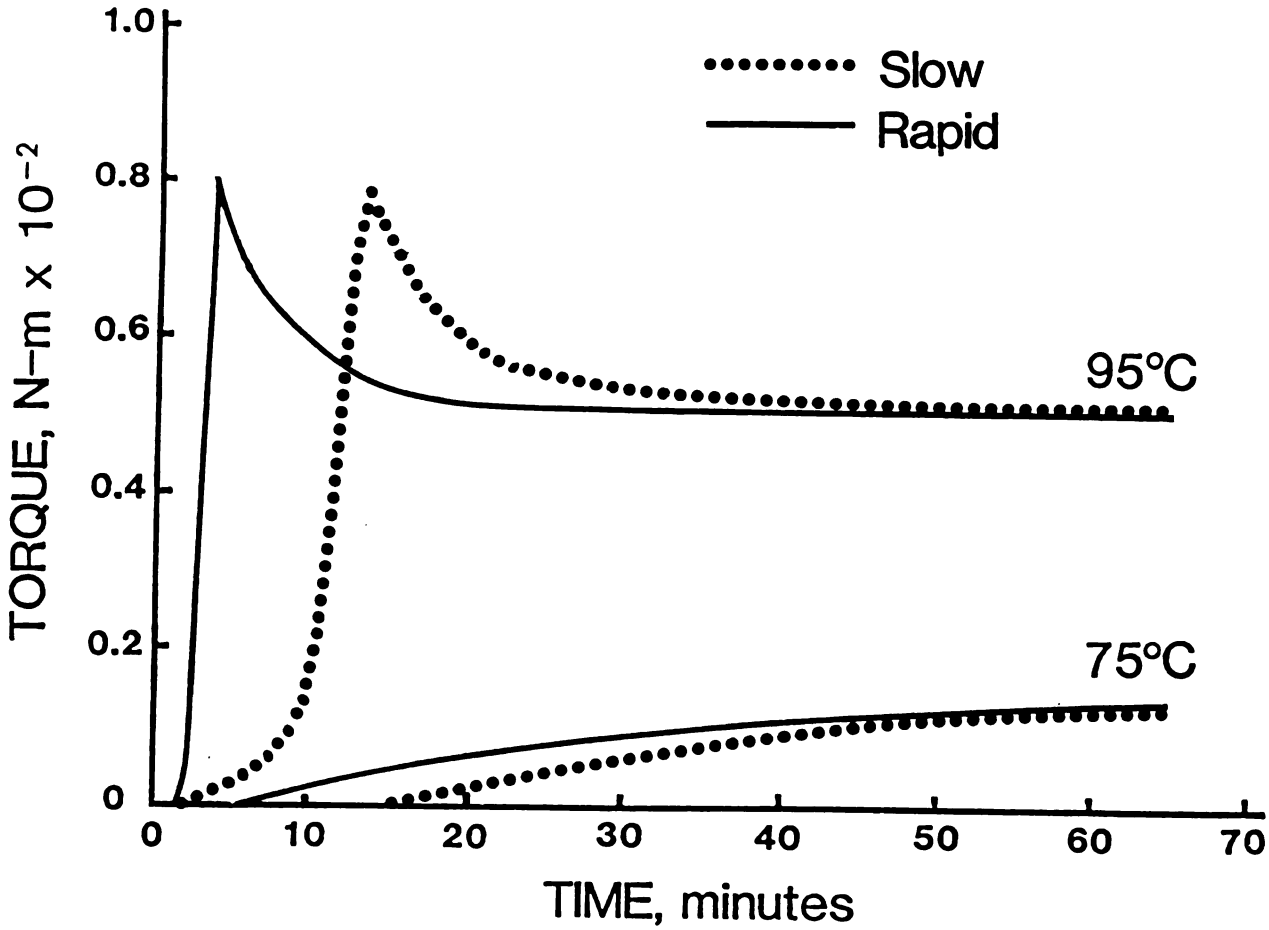


Figure 21. Thermal response curves of 10% navy bean starch pastes cooked at 75°C and 95°C for up to 60 min at different heating rates

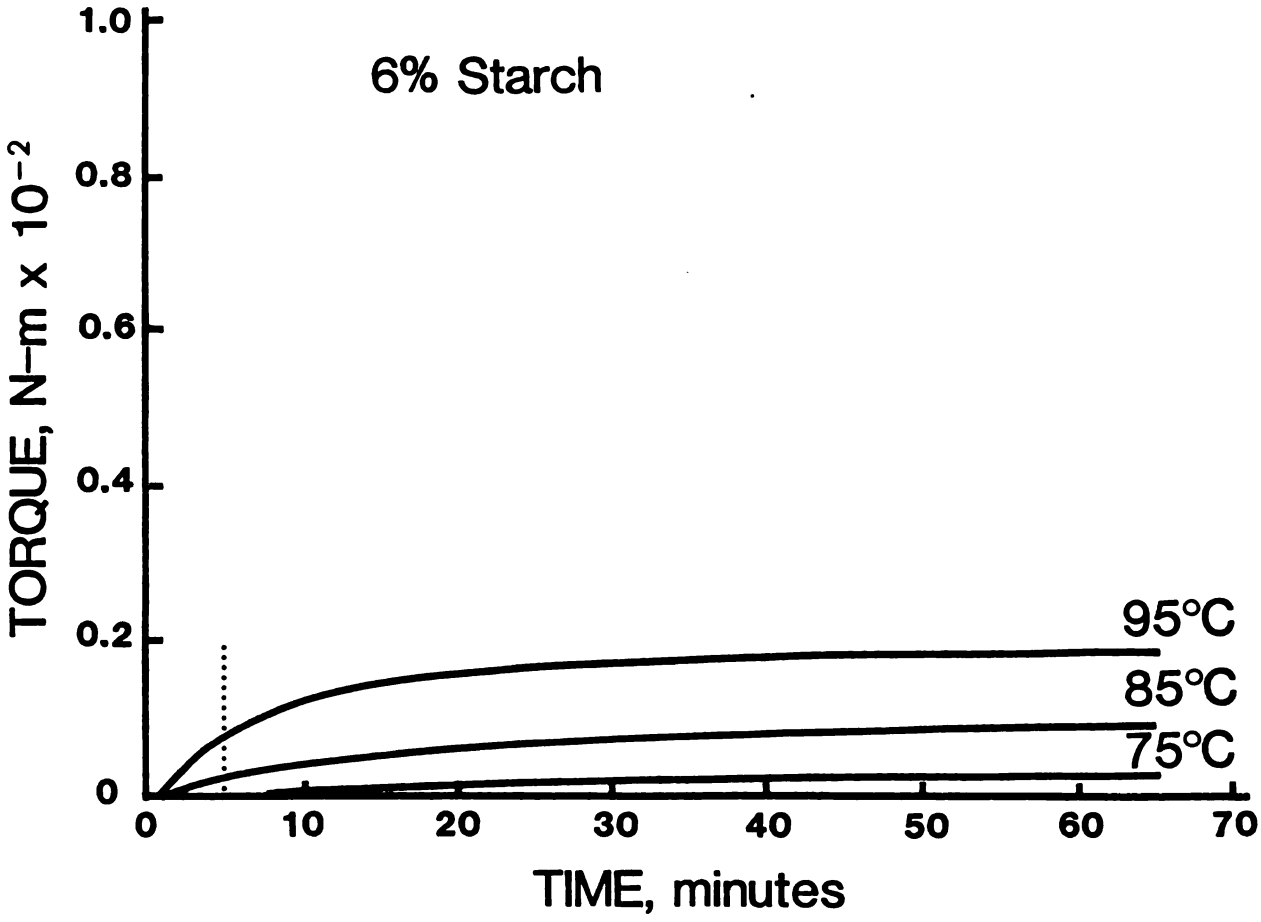


Figure 22. Thermal response curves of 6% navy bean starch pastes cooked at various temperatures for up to 60 min (vertical dotted line indicates come-up time to specified temperature)

time at which the starch pastes reached the respective cooking temperatures from 25°C. There was virtually no increase of the viscosity during heating from 25°C to 75°C. A slight viscosity increase, although very insignificant, was detected during cooking at 75°C and this process reached an equilibrium after about 40 min of cooking under constant shearing. Heating at 85°C and 95°C, the viscosities of the pastes increased relatively faster as can be seen from the elevated torque values. The viscosities of the pastes continued to increase during cooking at the high temperatures and approached equilibrium after about 40 min of cooking time. These thermal response curves indicated that 75°C cooking temperature was not sufficiently high enough to cause gelatinization or swelling of starch granules to a great extent. At higher temperatures the starch granules swelled more freely to give increased viscosities; however, the concentration was still too low to cause any visible mechanical breakdown of the granules due to shear.

Increasing the starch concentration to 8% resulted in dramatic increases of the viscosity for pastes cooked at the temperatures used (Figure 23). No viscosity change was observed for paste heated from 25°C to 75°C, indicating that starch granules did not gelatinize before this temperature was reached. A smooth viscosity increase was found for pastes heated from 25°C to 85°C. While maintaining an 85°C cooking temperature, the viscosity continued to increase and reached an equilibrium after about 30 min of cooking. Contrary to this, an abrupt increase of the viscosity was observed for paste heated from 25°C to 95°C. This paste viscosity was found to continue to increase for a few minutes after reaching 95°C and was followed by a gradual decline which ended with a final torque value lower than that of the paste heated at 85°C. The decrease in viscosity at 95°C was due to structural breakdown of the granules during shearing.

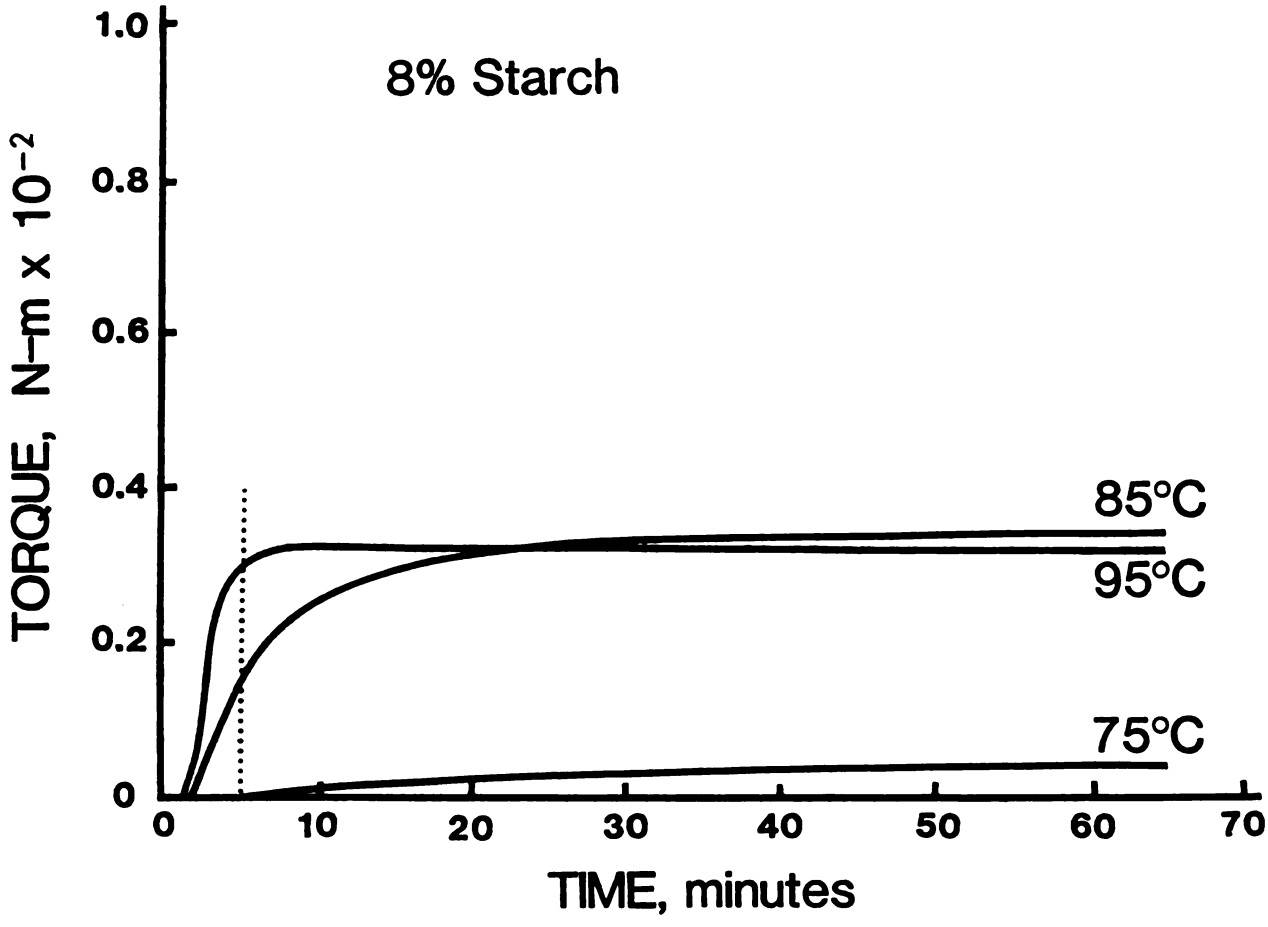


Figure 23. Thermal response curves of 8% navy bean starch pastes cooked at various temperatures for up to 60 min (vertical dotted line indicates come-up time to specified temperature)

It is recognized that when the starch suspension is heated above the gelatinization temperature the granules imbibe significant amounts of water, swell to many times their sizes, and impart considerable viscosity to the system.

The extent of gelatinization of starch granules cooked at 95°C was expected to be higher than that of the granules cooked at 85°C and, therefore, was expected to give higher viscosity. On the other hand, the less swollen granules at 85°C cooking temperature were much more rigid and less deformable than the highly swollen granules at 95°C. The higher paste viscosity at 85°C could possibly be attributed to these less swollen granules. It was suspected at this point that the increased starch concentration also played an important role in causing lower viscosities at higher temperatures. The final torque value of the 85°C was not much higher than that of 95°C. This could be due to the fewer granules that swelled under 85°C cooking.

Figure 24 shows a smooth but much faster viscosity increase for 10% starch at 75°C which gave a final torque value about three times higher than that of 8% starch. A significant increase of the viscosity was obtained for 10% starch suspension heated from 25°C to 85°C. This curve was similar to that of 8% starch cooked at 95°C. Thixotropic breakdown of the system was observed for the highest cooking temperature. A peak viscosity, with the torque value of 0.008 N-m, developed before the paste reached 95°C. This peak was followed by a continuous decrease, approaching an equilibrium torque value of 0.005 N-m during constant shearing. The curve obtained from 95°C indicated that maximum swelling of the granules, which resulted in the highest viscosity, occurred at the temperature before 95°C. At this temperature or higher, the highly swollen granules in the system were fragile and readily deformed and,

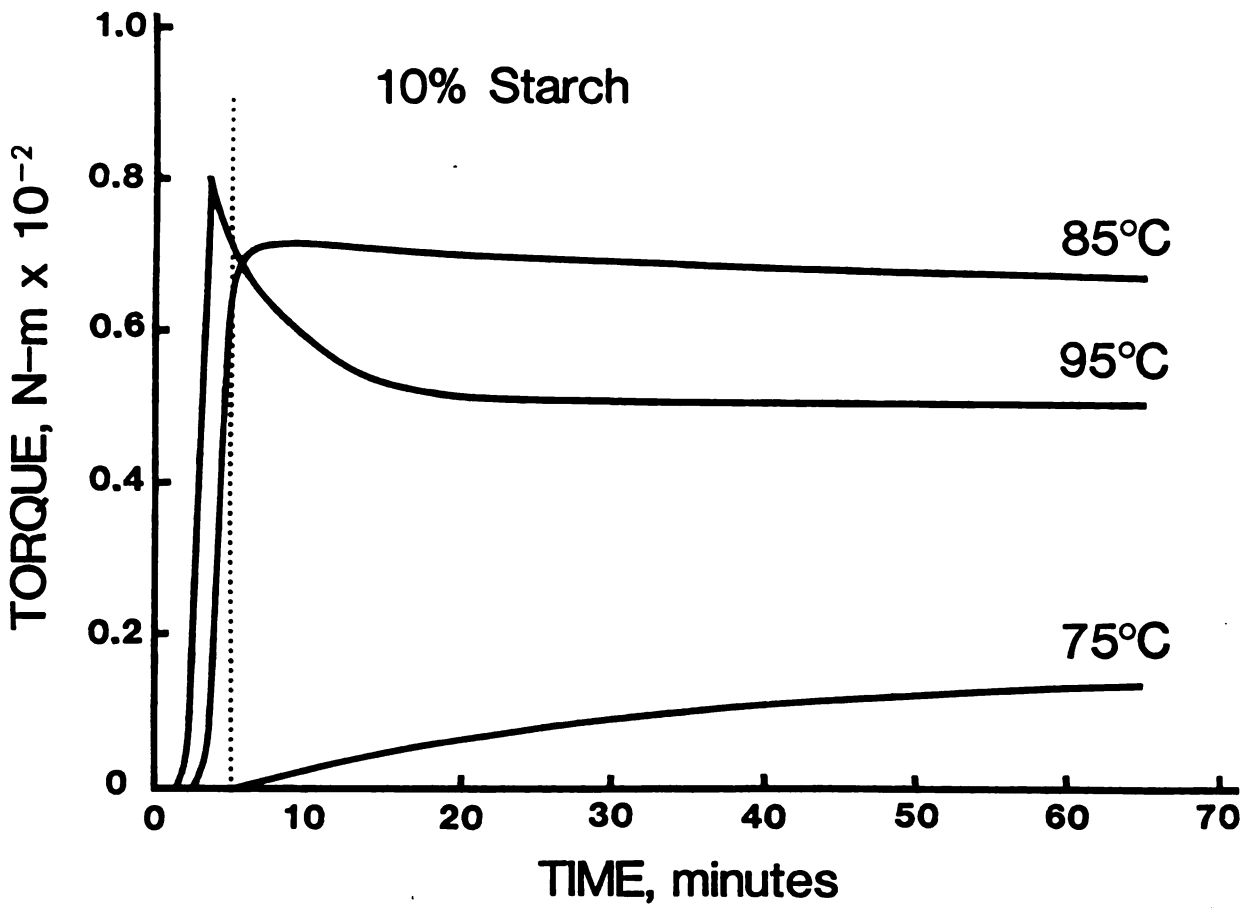


Figure 24. Thermal response curves of 10% navy bean starch pastes cooked at various temperatures for up to 60 min (vertical dotted line indicates come-up time to specified temperature)

therefore, were very susceptible to mechanical breakdown, leading to a significant reduction of the viscosity.

The abrupt changes in rheological properties, characteristic of gelatinized starch suspensions at a particular concentration, have been reported in systems such as polymer microgels (Shashoua and Beaman, 1958). Evans and Haisman (1979) studied the gelatinized starches and showed that significant viscosity effects occur only above a threshold concentration.

High starch concentration caused deformation of swollen granules at 95°C as can be seen from Figures 23 and 24. This was mainly due to the fact that flow occurs by particles deforming and thereby moving past each other without volume changes. It was believed that the threshold concentration as reported by Evans and Haisman (1979) was related to this study and was in the range of about 8% to 10% for the two higher temperatures tested.

At 12% starch concentration the final torque value for 75°C was about five times as high as that obtained from 10% concentration (Figure 25). A possible explanation could be that 12% starch paste cooked at 75°C for 60 min had reached a threshold point at which the swollen granules filled the total volume of the system, resulting in sufficient flow resistance to give a high final torque value.

Peak viscosities appeared at both 85°C and 95°C cooking; these peaks were followed by significant declines of the torque values due to deformation of the crowded granules at constant flow. It is worthy to note that the excessive swelling of the granules at 95°C cooking, which gave an earlier peak than did those at 85°C, resulted in more rapid and extensive thixotropic breakdown due to greater bond weakening within their structures.

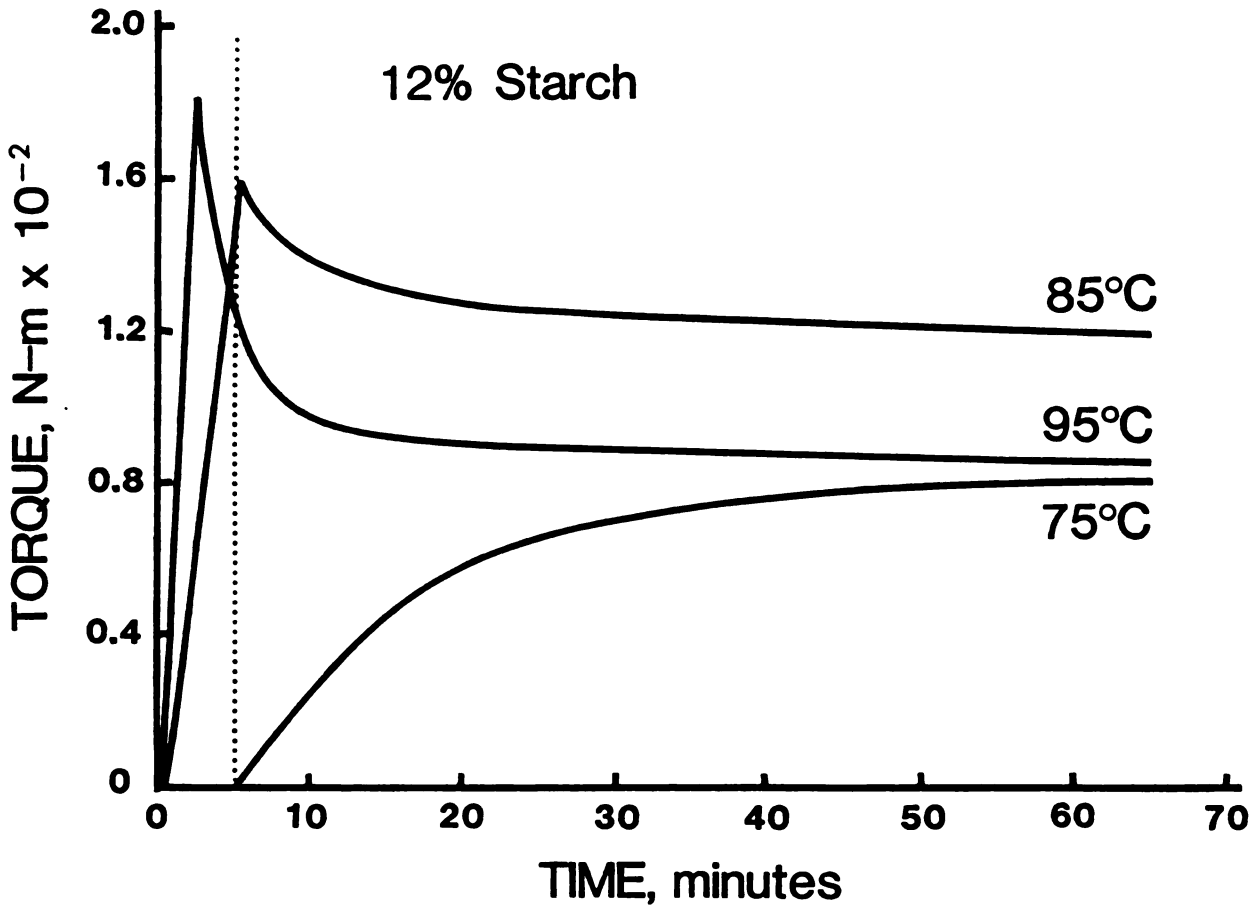


Figure 25. Thermal response curves of 12% navy bean starch pastes cooked at various temperatures for up to 60 min (vertical dotted line indicates come-up time to specified temperature)

Activation Energy in Starch Gelatinization

The gelatinization rate of rice and potato starches was studied by Kubota et al. (1979) using rheological methodology. In their study, a capillary tube viscometer was used to measure the flow behavior of heated starch suspensions at temperature ranges of 70°C to 80°C for rice starch and 60°C to 63°C for potato starch. This method appeared to be tedious in calculation of the rate constants for starch gelatinization and the preparation procedure of starch pastes remained questionable.

The technique developed in the current study afforded a continuous monitoring of the starch gelatinization process during cooking using the perforated paddle mixer at a constant speed of 50 rpm as described in the experimental section. It was judged, from the thermal response curves studied earlier, that 8% starch paste gave smooth increase of curves up to 85°C and was suitable for the gelatinization rate study. Four temperatures (75°C, 80°C, 85°C, and 95°C) were used to cook the starch pastes and the torque responses or torque values (M) were recorded from zero time, at which pastes reached the desired temperatures, up to 240 min (Figure 26). Torque values increased with increased gelatinization times and temperature, confirming that the gelatinization reactions proceeded in the regions covered.

Differences between the initial torque value (Mo), at time zero, and the maximum torque value (Mm) indicated the extent of gelatinization which occurred at each temperature. The ungelatinized portion of the paste at a certain cooking time (t) can, therefore, be expressed as (Mm-M)/(Mm-Mo). Assuming a first order reaction in the starch gelatin-

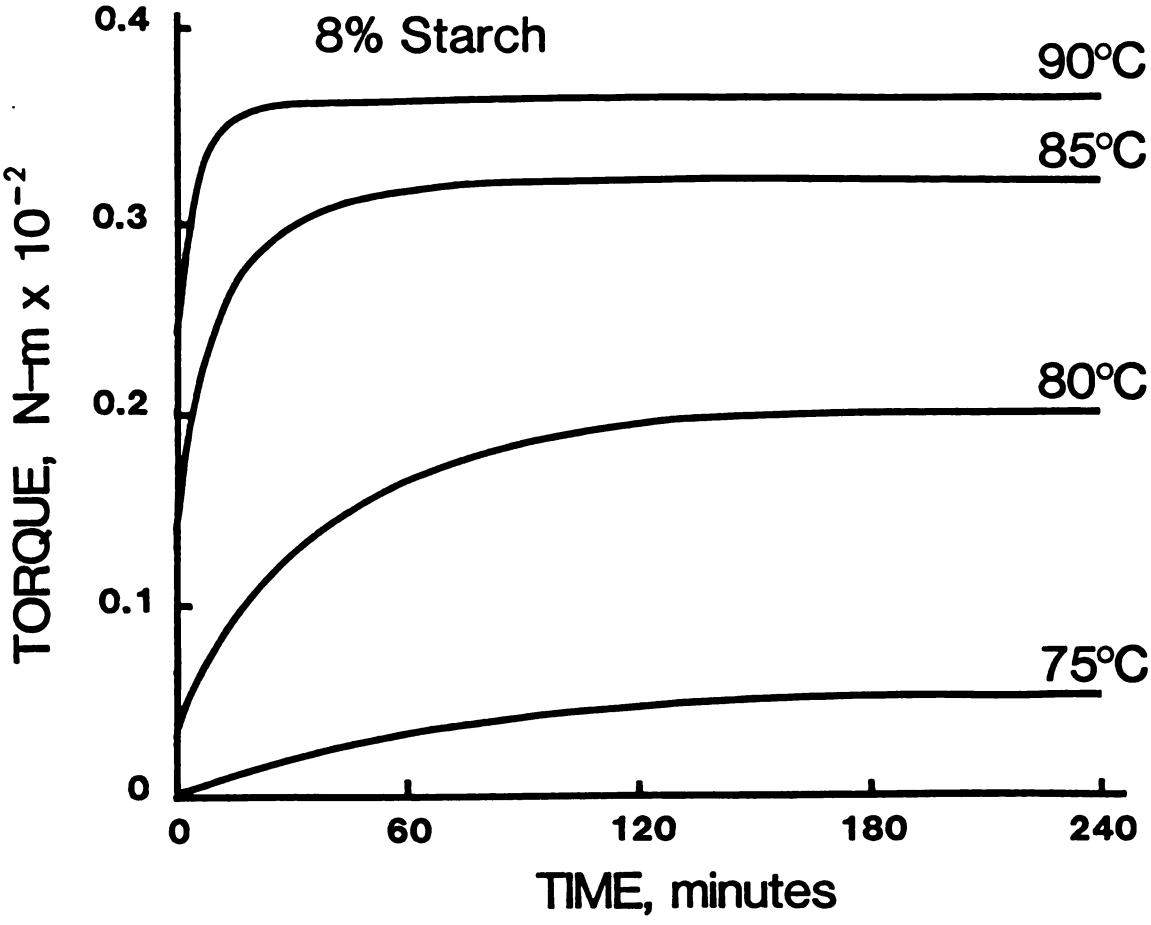


Figure 26. Thermal response curves for 8% navy bean starch pastes cooked at various temperatures for up to 240 min

ization (Kubota et al., 1979; Bakshi and Singh, 1980), the gelatinization rate constants at various temperatures could be calculated according to Equation 22 and are presented in Table 12:

$$\ln \frac{Mn - M}{Mn - Mo} = -kt \qquad (22)$$

Table 12. First order reaction kinetics of navy bean starch gelatinization at various cooking temperatures

Temperature (°C)	Reaction Rate Constant (1/min)	r^2
75	0.0182	0.985
80	0.0255	0.987
85	0.0324	0.992
90	0.0493	0.989

These rate constants are plotted on a semilogarithmic paper against the reciprocal of the absolute temperature (Figure 27) and a linear relationship was found between these two variables. The Arrhenius equation was, therefore, used to calculate the activation energy which was found to be 14.5 Kcal/g.mole.

The activation energy for cooking white rice as reported by Suzuki et al. (1976) was 1.9 Kcal/g.mole at 75°C to 100°C. Bakshi and Singh (1980) obtained a value of 18.5 Kcal/g.mole for rough rice at 50°C to 85°C and a value of 24.6 Kcal/g.mole for brown rice at the same

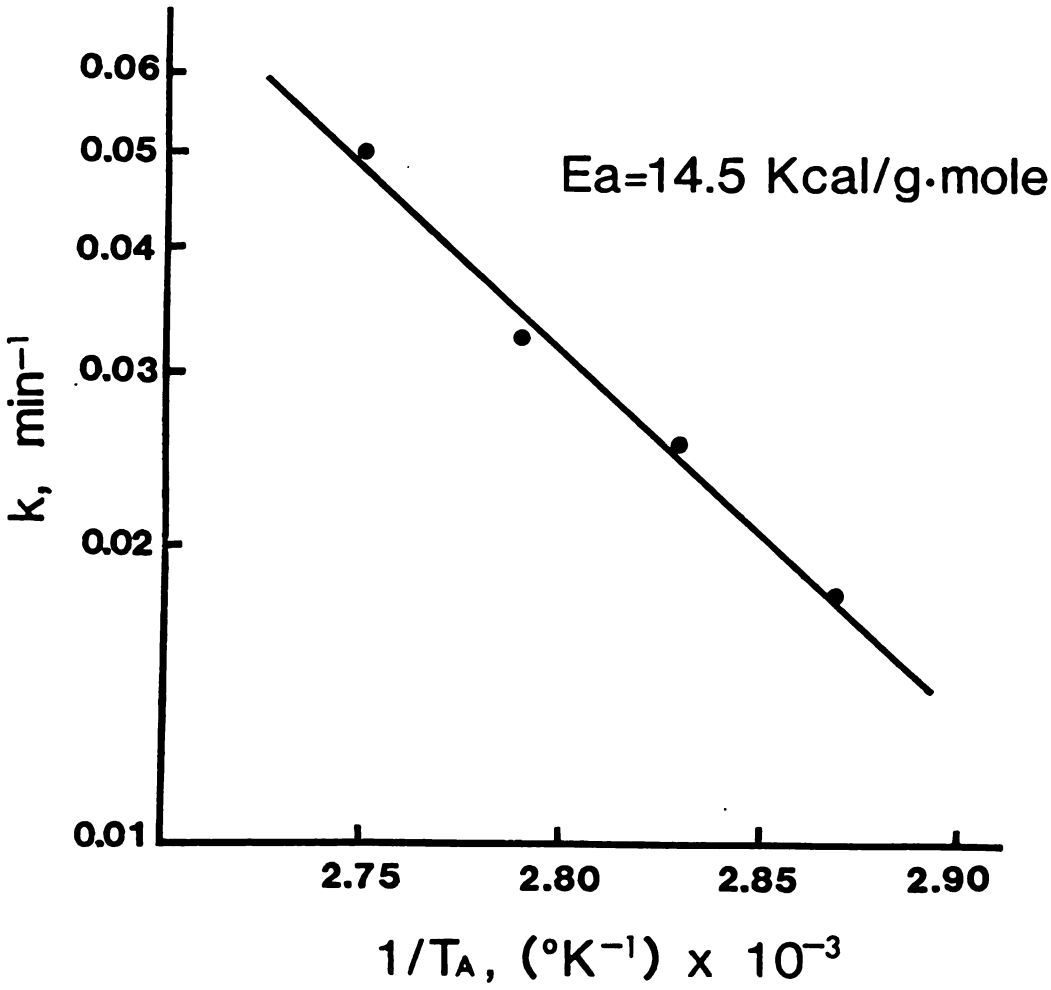


Figure 27. Arrhenius plot for the gelatinization rate constants of purified navy bean starch pastes

temperature range. Kubota et al. (1979) studied the gelatinization rate of rice starches and found the activation energy to be 14 Kcal/g.mole at 70°C to 85°C. The activation energy for the gelatinization of navy bean starch obtained in this study is within the range as reported by other researchers.

Yield Stress of Starch Pastes

Rheological measurements were conducted with an MV1 sensor (bob and cup) system. Yield stress was first evaluated and followed by a complete characterization of the flow curve for each starch paste sample.

After starch pastes had sheared for 60 min during cooking, the system became time independent and isothermal with shearing for a certain period of time at the range of shear rates used. As an example, Figure 28 illustrates the time independency of the cooked and sheared pastes when sheared at constant rates ranging from 1 rpm to 100 rpm which were the shear rates used for measuring pasted rheological properties.

Yield stress in a hydrocolloid system, such as starch paste, is commonly known as the stress to initiate flow. Various methods in measuring yield stress values in hydrocolloidal dispersions and some commercial semi-liquid foods have been used and discussed (Robinson-Lang and Rha, 1981; Canovas and Peleg, 1983). However, the experimental determination of this rheological parameter has not yet been satisfactorily investigated. With the use of a speed programmer, allowing a linear increase of the rotor speed from 0 rpm to 1 rpm, yield stress could be detected at the very first movement of the rotor. Since the yield stress after shearing can be expected to be smaller due to the

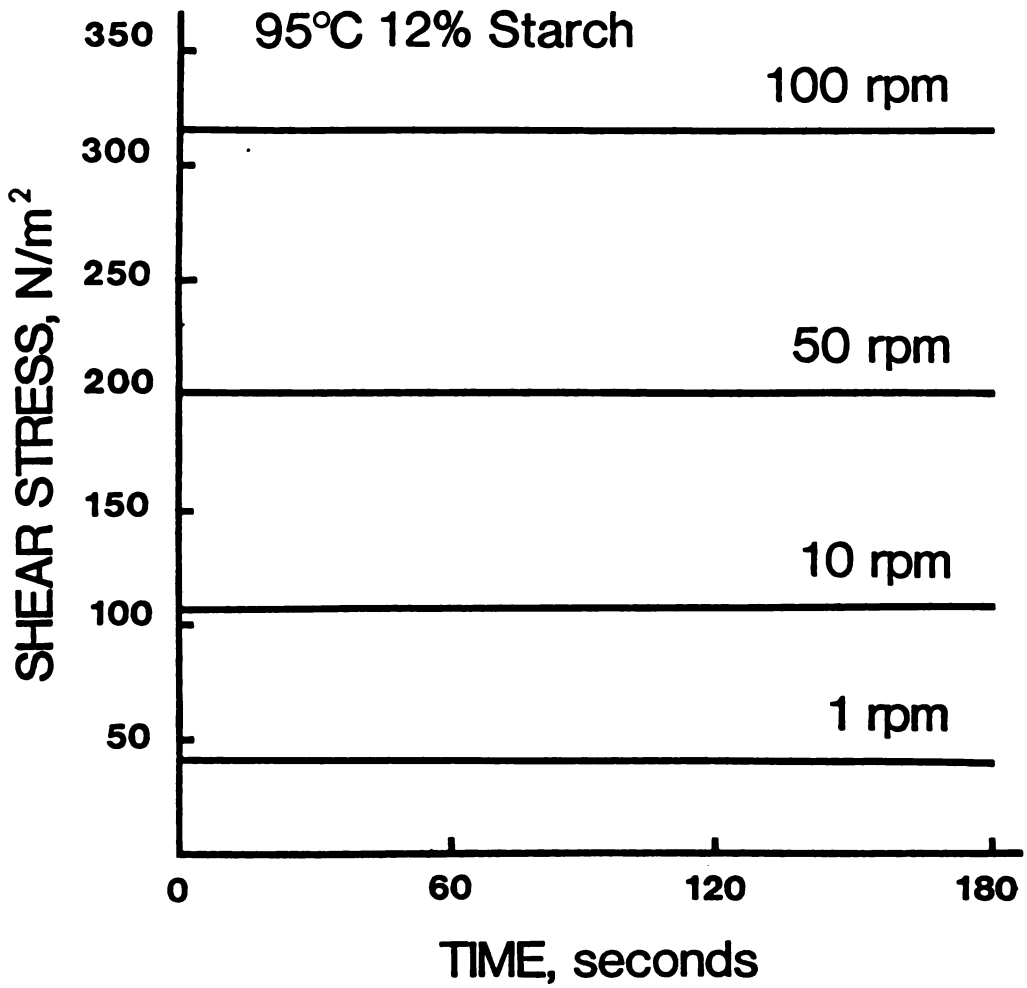


Figure 28. Determination of time independency with constant shearing at various rotation speeds for 12% navy bean starch pastes cooked at 95°C for 60 min while being mixed using a paddle speed of 50 rpm

disruption of the paste structure, it was recorded again after the shearing cycle. Results of the preliminary tests have indicated that these two values were identical for most samples. The magnitude of the yield stress (τ_y) obtained from this direct measurement for each treatment was compared with the yield stress (τ_o and K_o^2) obtained from curve fitting of the flow data with Herschel-Bulkley and Casson models. This will be discussed after the characterization of the flow curves.

Characterization of the Flow Curves

For the determination of flow curve, torque values were measured from the sample at one shearing cycle of rotor speeds, first in an ascending order and followed by a descending order to account for the thixotropic effect. Preliminary runs indicated that the two torque values from the up and down curves registered at each rotor speed were not significantly different for the samples tested and therefore only the values from the ascending curve were recorded for flow study. The raw and computed data, including yield stress, for only the starch pastes (6%, 8%, 10%, and 12%) cooked at 95°C are presented in Appendix Tables 17 through 26. Appendix Tables 17 through 20 represent the flow data obtained from the starch pastes after cooking at 95°C for 60 min. In order to examine the retrogradation of starch pastes, samples were cooked at 95°C and cooled to 50°C and the flow data were recorded (Appendix Tables 21 through 24). Further holding of the cooled pastes for 30 min at 50°C allowed for the evaluation of paste stability. Appendix Tables 25 and 26 show the flow data for 6% and 8% pastes. Gel formation was found for pastes with 10% and 12% concentrations and therefore, no data were reported. This gel formation was also found for the cooled pastes initially cooked at 85°C in this study.

Figure 29 illustrates the typical flow curves obtained from HP 85 output for each sample concentration cooked at 95°C. The flow data were fitted to power law, Herschel-Bulkley (with and without a given yield stress), and Casson models to obtain the rheological parameters.

Rheological Parameters of Starch Pastes

Hot Pastes. Mean values and Tukey mean separations for the rheological parameters obtained by curve fitting the experimental data to the selected flow models for starch pastes after cooking at various temperatures for 60 min are presented in Table 13. Statistical analysis of these data are summarized in Appendix Table 27.

Significant main effect differences in the values of yield stress (τ_y, τ_o, and K_o^2), consistency index (K), and flow behavior index (n) were detected for cooking temperature and starch concentration. Due to the significant interactions of the temperature and concentration, each temperature was analyzed separately with a one-way classification method.

For the power law model, K values of the pastes cooked at different temperatures increased significantly with increasing starch concentration indicating that pastes with higher consistency or viscosity could be produced by increasing starch content. The highest viscosities were obtained with the pastes cooked at 85°C with concentrations greater than 8%. Significant changes of the n values were found when the starch concentration increased from 10% to 12% at 75°C and from 6% to 8% or higher at 85°C; however, the n values remained constant for pastes cooked at 95°C at different concentrations. These gelatinized starch pastes exhibited pseudoplastic behavior over the range of shear rates tested.

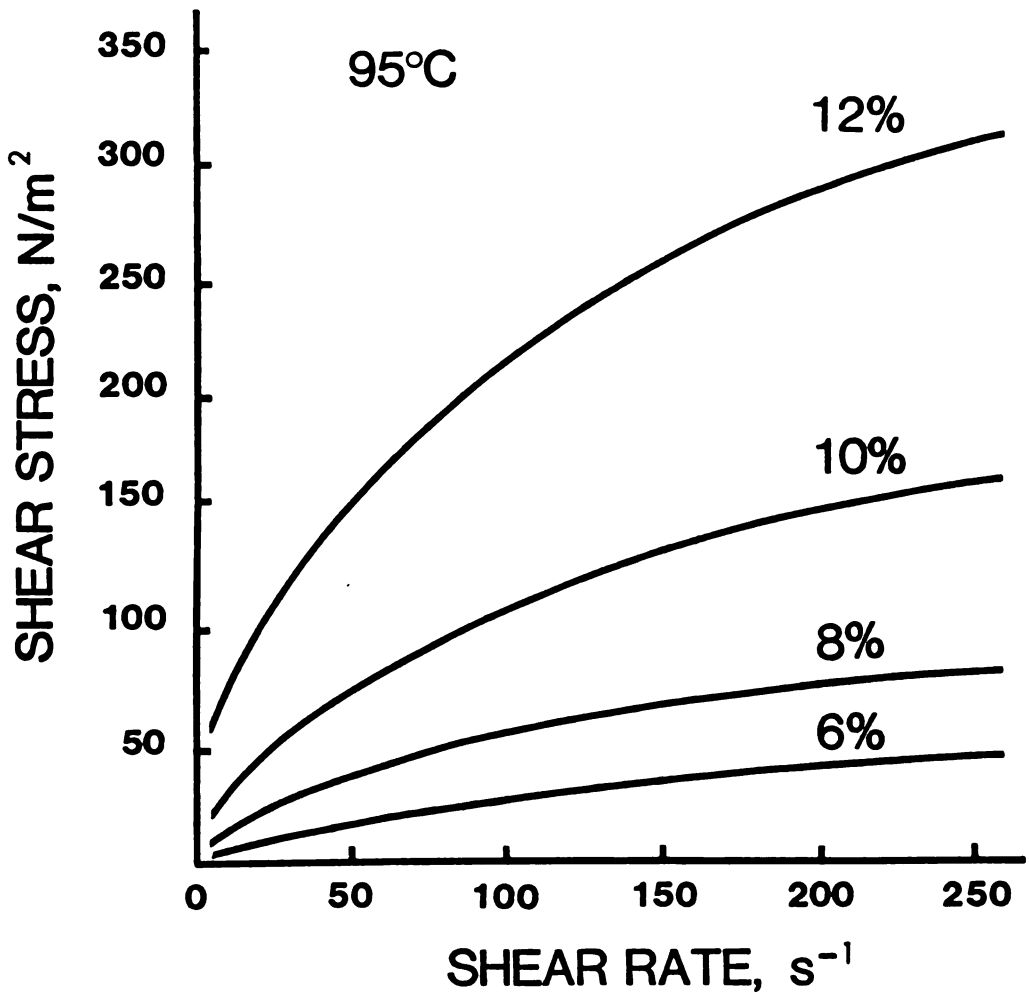


Figure 29. Flow curves for navy bean starch pastes of various concentrations cooked at 95°C for 60 min

Table 13. Rheological parameters computed from selected flow models for navy bean starch pastes of various concentrations cooked at 75°C, 85°C, and 95°C for 60 min prior to measurements with the Haake Viscometer[1,2]

Treatment Temp, Conc (°C, %db)		Power Law		Herschel-Bulkley[3]			Herschel-Bulkley[4]			Casson	
		K	n	τ_y	K	n	τ_o	K	n	K_o^2	K_c
75	6	0.05a	0.794b	0.00a	0.05a	0.794b	0.00a	0.09a	0.761d	0.01a	0.09a
	8	0.10a	0.724b	0.00a	0.10a	0.724b	0.00a	0.30b	0.721c	0.27a	0.15a
	10	1.62b	0.720b	0.25b	1.32b	0.728b	0.11b	2.08c	0.684b	3.99b	0.24b
	12	5.86c	0.567a	2.05c	4.67c	0.611a	1.96c	5.32d	0.582a	9.80c	0.54c
85	6	0.35a	0.740b	0.00a	0.35a	0.740b	0.00a	0.64a	0.600c	0.50a	0.24a
	8	6.83b	0.444a	3.30b	4.68b	0.513a	2.09b	7.45b	0.422a	10.16b	0.38b
	10	16.08c	0.443a	8.30c	10.81c	0.514a	4.60c	13.54c	0.466b	23.14c	0.59c
	12	36.65d	0.437a	14.79d	26.73d	0.496a	12.24d	39.15d	0.452b	45.97d	0.99d
95	6	2.89a	0.464a	0.59a	2.52a	0.488a	0.00a	3.06a	0.448b	4.27a	0.27a
	8	6.79b	0.438a	1.93b	5.22b	0.487a	1.50b	7.02b	0.423a	10.07b	0.36b
	10	13.43c	0.437a	6.70c	8.89c	0.496a	10.94c	7.27b	0.539d	19.10c	0.53c
	12	26.95d	0.443a	11.14d	20.02d	0.491a	11.18d	20.07c	0.490c	37.55d	0.78d

[1]Mean values (like letters within each column for each temperature indicate no significant differences at $P < 0.05$ by Tukey mean separation; $n = 3$)

[2]Units for rheological parameters: K ($N \cdot s^n/m^2$); n (dimensionless); τ_y, τ_o, K_o^2 (N/m^2); K_c ($N \cdot s/m^2$)$^{0.5}$

[3]With given yield stress (τ_y) from direct measurement

[4]Non-linear curve fitting

Yield stress was not detected for hot pastes of 6% and 8% at 75°C or of 8% at 85°C. For the pastes showing yield stress, the values increased significantly with increased concentration at each temperature (Table 13). Pastes cooked at 75°C produced the lowest yield values for all concentrations. The pastes cooked at 85°C were found to have significantly higher τ_y and K values than those cooked at 95°C for starch concentrations of 10% and 12%. When fitting the flow data to the Herschel-Bulkley model with the given yield stress, K and n values were obtained and found to have a similar trend as those obtained from the power law model. Higher K and lower n values were obtained from the power law model than those from this model.

Duran and Costell (1982) studied the rheology of apricot puree and found the same differences in these two flow parameters. They reasoned that the energy used to destroy the network structure of the plastic material having a yield stress was included as part of the shear response of the material when power law was used.

When fitting both the power law and the Herschel-Bulkley equations to the experimental data, high r^2 values were obtained as shown in Appendix Table 28, although the former had higher r^2 values than the latter for all the treatments. The good fit of these two models was further confirmed by plotting the data on the log τ versus log $\dot{\gamma}$ and log $(\tau - \tau_y)$ versus log $\dot{\gamma}$ as illustrated in Figures 30 and 31. Although the linear regression curve for the power law plot seems to be a better fit than that of the Herschel-Bulkley plot, which resulted in higher r^2 values, from a rheological point of view, the latter is a more appropriate model for characterization of the starch paste especially when the sample exhibits a yield stress. However, it is still valuable to obtain the rheological parameters using the power law model due to its simplicity.

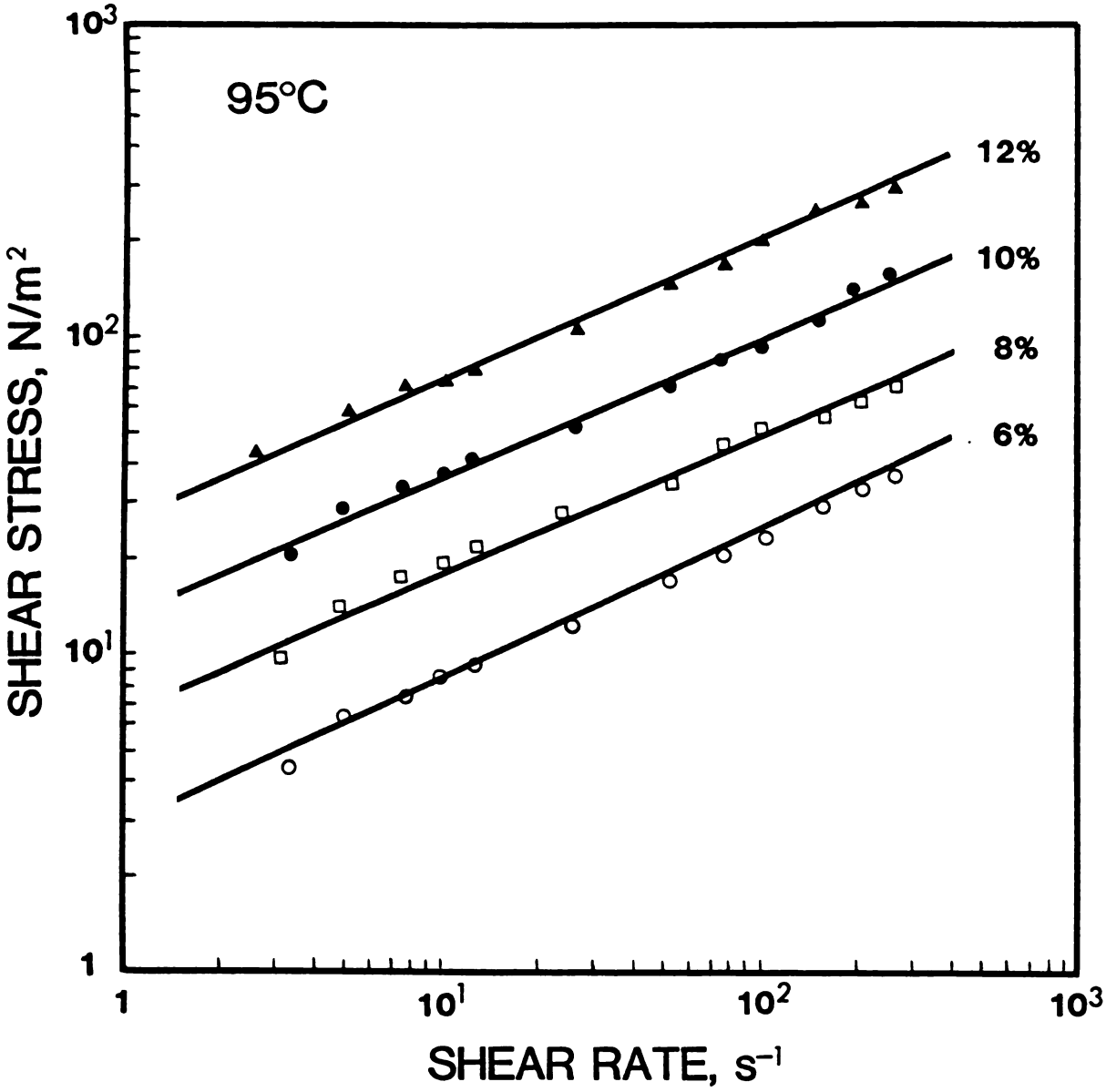


Figure 30. Power law plot of the flow data for navy bean starch pastes of various concentrations cooked at 95°C for 60 min

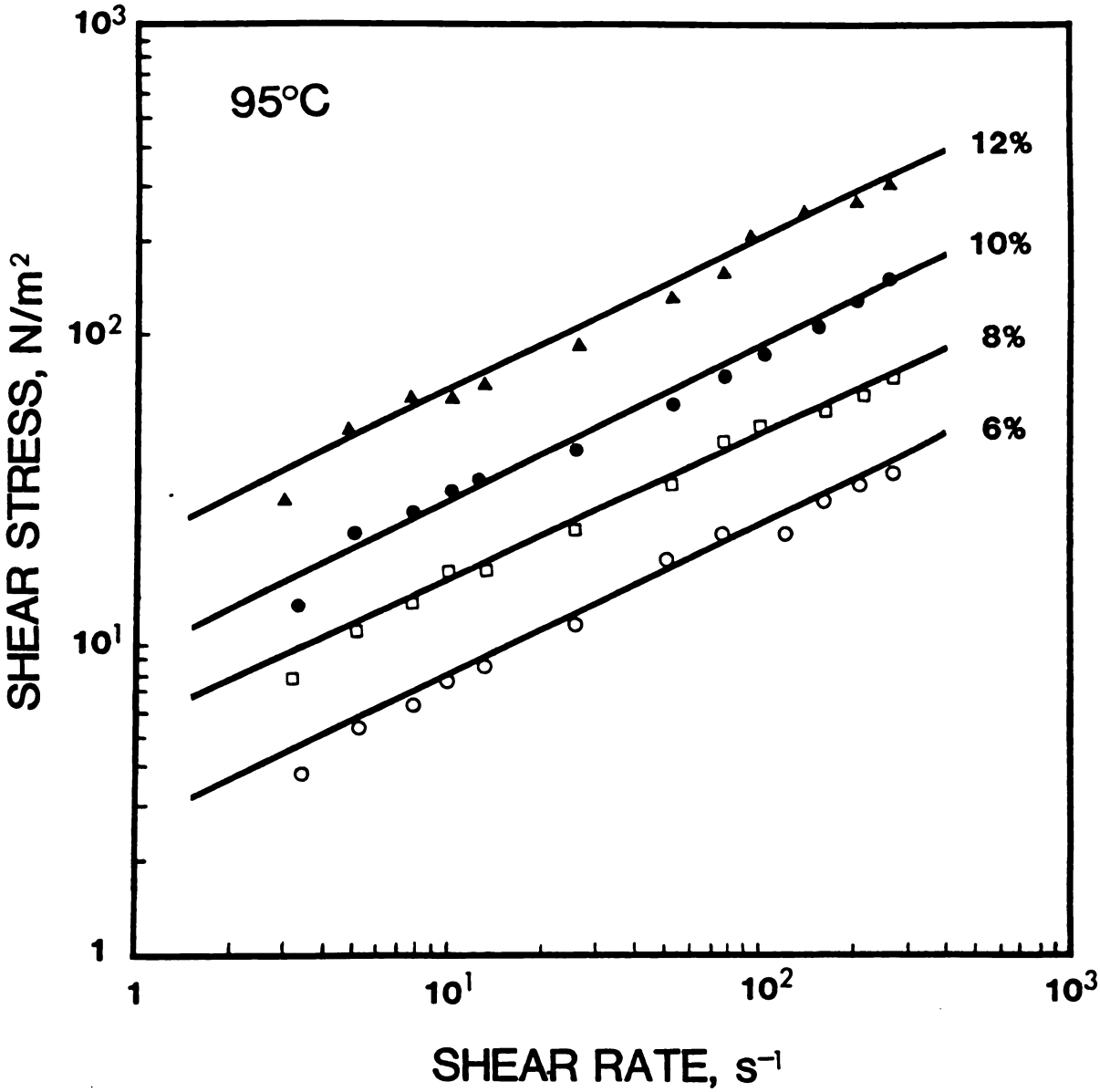


Figure 31. Herschel-Bulkley plot of the flow data for navy bean starch pastes of various concentrations cooked at 95°C for 60 min

The application of the Herschel-Bulkley model using non-linear regression analysis to obtain the three parameters, τ_o, K, and n, was studied. The yield stress and consistency index generally increased with increasing concentration (Table 13). This method gave satisfactory estimations for these parameters when compared to those obtained from the previous method with the exception of those for 85°C at 8% and 95°C at 10%.

Casson model was designed to characterize the flow behavior of biphasic disperse systems in which the interacting particles are dispersed in a Newtonian medium (Casson, 1959). This model has been used to describe the flow behavior of tomato concentrates (Charm, 1963b; Rao et al., 1981), chocolate (Chevalley, 1975), fruit purees (Duran and Costell, 1982; Vitali and Rao, 1982), and some commercial semi-liquid foods (Canovas and Peleg, 1983). Its applicability to navy bean starch pastes was studied to evaluate the magnitude of the consistency index (K_c) and the Casson yield stress (K_o^2) for comparison with the yield stress from direct measurement.

High r^2 values ($r^2 > 0.9676$) were obtained when fitting the Casson model equation to the experimental data for starch pastes of four concentrations cooked at 95°C (Figure 32). The r^2 values for the samples tested, in fact, had magnitudes in the range of 0.8472 to 0.9826 throughout the experiment as shown in Appendix Table 28. Despite the high correlation coefficients, the deviation of the experimental points in the lower shear rate range and the fact that the Casson yield values were considerably greater than the measured yield values for most of the treatments (Table 13) indicated that the application of this model was not quite satisfactory.

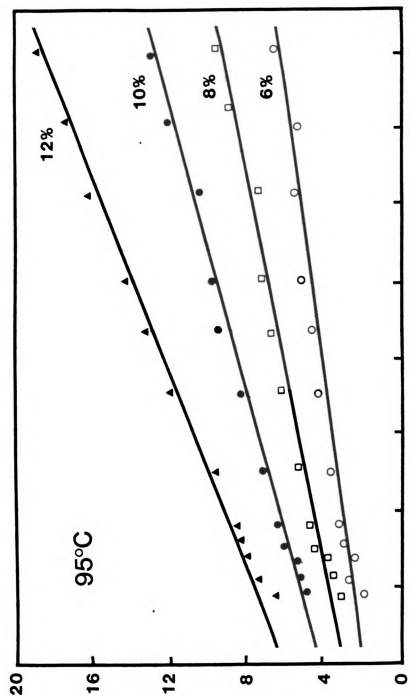


Figure 32. Casson plot of the flow data for navy bean starch pastes of various concentrations cooked at 95°C for 60 min

Cooled Pastes. The flow data of cooled pastes were analyzed as discussed for the hot pastes. Mean values and Tukey mean separations for the rheological parameters of the cooled starch pastes at 50°C are presented in Table 14. Statistical analysis of these data are outlined in Appendix Table 29. Analysis of variance indicated that the main effects and their interactions were highly significant for all the parameters listed. One-way classification analysis was used to examine the effect of concentration for each temperature due to the significant interaction.

Similar to discussions of hot pastes, comparisons among the flow models, used for obtaining the rheological parameters, showed that the Herschel-Bulkley model with given yield values appeared to be the most appropriate one to characterize flow behavior of the cooled starch pastes.

No yield stress was measured for cooled pastes of 6% and 8% at 75°C or at 8% at 85°C. Pastes exhibiting yield stress showed yield values to increase significantly with increased concentration for each cooking temperature. The K values increased significantly with increased concentration. Cooled pastes with concentrations of 10% and 12% cooked at 85°C were shown to give significantly higher τ_y and K values than those cooked at 95°C. The n values decreased significantly as the concentrations increased from 10% to 12% at 75°C and from 6% to 8% or higher at 85°C, whereas at 95°C this parameter did not change with concentration (Table 14).

It is interesting to note that there was a linear relationship between the concentration and the square root of yield stress for the hot and the cooled pastes (Figure 33). This type of relationship has

Table 14. Rheological parameters computed from selected flow models for navy bean starch pastes of various concentrations cooked at 75°C, 85°C, and 95°C for 60 min and cooled to 50°C prior to measurements with the Haake Viscometer[1,2]

Treatment Temp,Conc (°C, %db)		Power Law		Herschel-Bulkley[3]			Herschel-Bulkley[4]			Casson	
		K	n	τ_y	K	n	τ_o	K	n	K_o^2	K_c
75/50	6	0.08a	0.760b	0.00a	0.08a	0.760b	0.00a	0.10a	0.741d	0.04a	0.10a
	8	0.20a	0.739b	0.00a	0.20a	0.739b	0.00a	0.25a	0.723c	0.24a	0.18a
	10	0.75a	0.723b	0.31b	0.60b	0.724b	0.21b	0.66b	0.706b	1.08a	0.33b
	12	11.94b	0.457a	4.96c	8.57c	0.519a	4.42c	9.25c	0.495a	19.09b	0.52c
85/50	6	0.95a	0.606b	0.00a	0.95a	0.606b	0.00a	1.31a	0.532b	1.45a	0.25a
	8	10.16a	0.435a	5.93b	6.33b	0.519a	3.25b	10.90b	0.418a	14.99b	0.45b
	10	31.35b	0.430a	15.49c	20.54c	0.497a	10.90c	20.33c	0.403a	44.53c	0.59b
	12	75.41c	0.430a	25.66d	55.56d	0.500a	22.41d	62.02d	0.408a	68.28d	1.84c
95/50	6	4.83a	0.442a	0.61a	4/43a	0.457a	0.72a	4.43a	0.454a	7.09a	0.32a
	8	15.63b	0.402a	4.87b	12.31b	0.443a	4.31b	9.30b	0.435a	21.35b	0.51b
	10	25.44c	0.401a	12.54c	12.23b	0.467a	9.32c	18.82c	0.449a	34.48c	0.64b
	12	47.94d	0.402a	22.30d	32.94c	0.469a	22.48d	34.41d	0.452a	60.69d	0.99c

[1]Mean values (like letters within each column for each temperature indicate no significant difference at $P < 0.05$ by Tukey mean separation; $n = 3$)

[2]Units for rheological parameters: $K(N \cdot s^n/m^2)$; n (dimensionless); τ_y, τ_o, $K_o^2(N/m^2)$; $K_c(N \cdot s/m^2)^{0.5}$

[3]With given yield stress (τ_y) from direct measurement

[4]Non-linear curve fitting

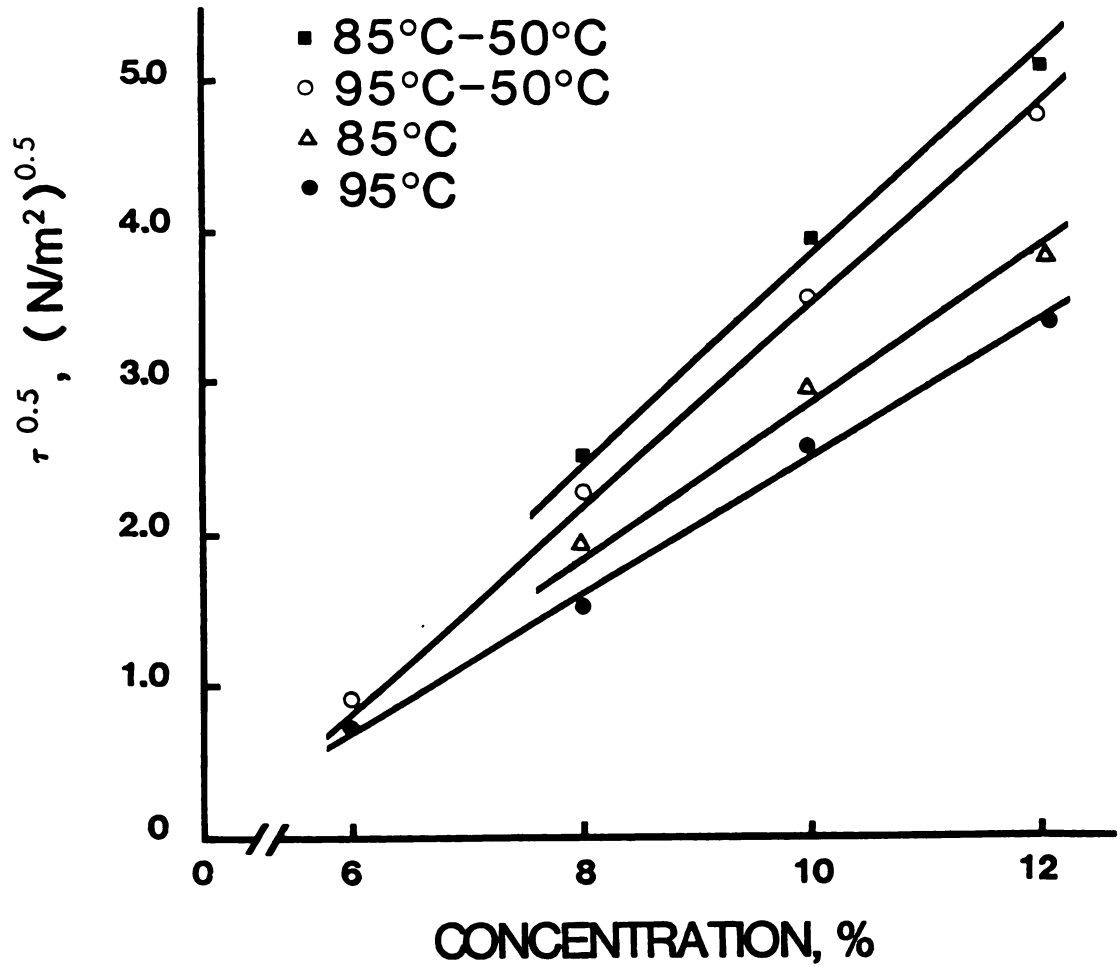


Figure 33. Relationship between the square root of yield stress and starch concentration for hot and cooled navy bean starch pastes

been reported for some colloidal suspensions (Firth and Hunter, 1976). Evans and Haisman (1979) used this relationship for various starches to find the concentrations for the initial development of yield stress. Extrapolation of these lines to the intercept in Figure 33 suggests that yield stress can be developed when cooking starch paste at 85°C or 95°C with the concentration about 4% to 5%.

To further evaluate the stability of starch pastes, the pastes at 50°C were held in the cup at the same temperature for an additional 30 min prior to flow measurements. Table 15 represents the mean values and statistical analysis for the rheological data of the cooled pastes. Pastes of 10% and 12% concentrations cooked at 85°C and 95°C were found to form gels after holding and thus flow measurements were not attained. The flow behavior of the paste at 75°C changed significantly when the concentration was found to have pronounced effect on τ_y and K values even at low levels.

In order to better show the effect of cooling and holding on the rheological properties of the cooked pastes, the measured yield values and the parameters obtained from the Herschel-Bulkley model are drawn from Tables 13, 14, and 15 and are presented in Table 16. Pastes with 10% concentration or lower, cooked at 75°C, or 6% concentration, cooked at 95°C, remained stable after cooking and holding. Strong retrogradation tendency, however, was shown for the starch pastes with concentrations of 12%, cooked at 75°C, and 8%, 10%, and 12%, cooked at 85°C and 95°C, as evidenced by the significant increase of the yield values with concomitant increase of the paste consistency.

In the gelatinization process amylose molecules leach from the swollen granules and enter the surrounding aqueous phase. If this swelling process reaches the point where the granules occupy the entire

Table 15. Rheological parameters computed from selected flow models for navy bean starch pastes of various concentrations cooked at 75°C, 85°C, and 95°C for 60 min, cooled to 50°C, and held at 50°C for 30 min prior to measurements with the Haake Viscometer[1,2]

Treatment Temp,Conc (°C, %db)		Power Law		Herschel-Bulkley[3]			Herschel-Bulkley[4]			Casson	
		K	n	τ_y	K	n	τ_o	K	n	K_o^2	K_c
75/50/50	6	0.09a	0.754c	0.00a	0.09a	0.755b	0.00a	0.19a	0.735c	0.06a	0.11a
	8	0.20a	0.741bc	0.00a	0.21a	0.740b	0.00a	0.22a	0.730c	0.23a	0.18b
	10	0.82a	0.720b	0.33b	0.58a	0.730b	0.25b	0.62b	0.695b	1.03a	0.32c
	12	11.13b	0.452a	5.21c	7.64b	0.522a	4.39c	10.04c	0.501a	18.79b	0.48d
85/50/50	6	1.18a	0.611b	0.00a	1.18a	0.611b	0.00a	1.30a	0.530b	1.70a	0.30a
	8	10.13b	0.441a	6.31b	6.12b	0.533a	3.29b	7.04b	0.413a	14.80b	0.46b
	10	---[5]	---	---	---	---	---	---	---	---	---
	12	---	---	---	---	---	---	---	---	---	---
95/50/50	6	4.58a	0.438a	0.65a	4.15a	0.455a	0.78a	4.55a	0.449b	6.41a	0.31a
	8	17.15b	0.389b	4.89b	13.83b	0.441a	4.30b	9.40b	0.431a	24.22b	0.49b
	10	---	---	---	---	---	---	---	---	---	---
	12	---	---	---	---	---	---	---	---	---	---

[1]Mean values (like letters within each column for each temperature indicate no significant difference at $P < 0.05$ by Tukey mean separation; $n = 3$)

[2]Units for rheological parameters: $K(N \cdot s^n/m^2)$; n (dimensionless); τ_y, τ_o, $K_o^2(N/m^2)$; $K_c(N \cdot s/m^2)^{0.5}$

[3]With given yield stress from direct measurement

[4]Non-linear curve fitting

[5]Unable to obtain flow data due to gel formation

Table 16. Rheological parameters computed from the Herschel-Bulkley model with given yield values for hot and cooled navy bean starch pastes[1,2]

Treatment Temp,Conc (°C, %db)		τ_y			K			n		
		Initial[3]	Cooled[4]	Held[5]	Initial	Cooled	Held	Initial	Cooled	Held
75	6	0.00a	0.00a	0.00a	0.05a	0.08a	0.09a	0.794b	0.760b	0.755b
	8	0.00a	0.00a	0.00a	0.10a	0.20a	0.21a	0.724b	0.739b	0.740b
	10	0.25b	0.31b	0.33b	1.32b	0.60b	0.58a	0.728b	0.724b	0.730b
	12	2.05c	4.96c	5.21c	4.67c	8.57c	7.64b	0.611a	0.519a	0.522a
85	6	0.00a	0.00a	0.00a	0.35a	0.95a	1.18a	0.740b	0.606b	0.611b
	8	3.30b	5.93b	6.31b	4.68b	6.33b	6.12b	0.513a	0.519a	0.533a
	10	8.30c	15.49c	---	10.81c	20.54c	---	0.514a	0.497a	---
	12	14.79d	25.66d	---	26.73d	55.56d	---	0.496a	0.500a	---
95	6	0.59a	0.61a	0.65a	2.52a	4.43a	4.15a	0.488a	0.457a	0.455a
	8	1.93b	4.87b	4.89b	5.22b	12.31b	13.83b	0.487a	0.443a	0.441a
	10	6.70c	12.54c	---	8.89c	17.23b	---	0.496a	0.467a	---
	12	11.14d	22.30d	---	20.02d	32.94c	---	0.491a	0.469a	---

[1]Mean values (like letters within each column for each temperature indicate no significant difference at $P < 0.05$ by Tukey mean separation; $n = 3$)

[2]Units for reheological parameters: τ_y (N/m^2); K ($N \cdot s^n/m^2$); n (dimensionless)

[3]Measured at cooking temperature

[4]Measured after pastes were cooled to 50°C

[5]Measured after pastes were cooled to 50°C and held for 30 min

volume, the amylose in the exudate will rediffuse into the swollen granules. Upon cooling, these molecules rebond to one another and to branches of amylopectin to establish a network in the system. As stated earlier, in the cooking process of the navy bean starch pastes, 12% for 75°C and 8% to 10% for 85°C and 95°C were thought to be the concentrations at which the flocculated swollen granules filled the entire volume with the rediffused amylose in the granules. As the pastes were cooled these molecules which were already present in the entire system caused the rapid and effective retrogradation process, leading to the significant increase of the paste yield stress and consistency values.

For most of the treatments, the flow behavior indices tend to decrease upon cooling of the pastes. This probably resulted from the rebonding and reentanglement of the molecules due to retrogradation process.

It was reported by Odigboh and Mohsenin (1975) that the greater the percentage of intact partially swollen granules in the system, the stronger the network of the paste structure, due to amylose binding with these granules in cold cassava starch paste. The fact that the yield stress and consistency index values were higher at 85°C than those at 95°C for the 10% and 12% cooled pastes (Table 16) further suggested that more granule disintegration occurred at 95°C than at 85°C at higher concentrations during cooking and shearing.

Pastes with concentrations 10% or higher, cooked at 85°C and 95°C, were shown to produce unstable cooled pastes at 50°C (Table 16). The excessive amount of amylose available in the system could lead to gradual precipitation, resulting in gel formation during the holding period.

SUMMARY AND CONCLUSIONS

Physicochemical characterization of the air-classified navy bean flours indicated that significant differences were shown for chemical composition of all flour fractions. HPLC sugar analysis showed that high protein flour contained the highest level of stachyose which was the major oligosaccharide for all fractions. Surface reflectance color measurement of bean flour indicated that cotyledon fractions (protein, starch) were lighter than hull flour. Farinograms showed that wheat flour substituted with 10% bean fractions resulted in increased water absorption and decreased mixing performance. Peak development time among fractions was similar. Mixing stability of hull flour was significantly lower than for the other fractions. Pasting characteristics of whole flour and high starch flours were demonstrated to be controlled swelling at high temperature. Slurries remained stable during high temperature holding, and upon cooling, showed moderate increase in viscosity. Dry-roasted navy bean flour fractions appeared to be suitable ingredients for use in appropriate food systems.

In the storage stability study, equilibrium moisture content (EMC) of flour fractions increased with increased water activity (a_w) from 0.48 to 0.97. EMC of high protein flour was the highest among all fractions while that of hull flour was the lowest at all a_w levels. Moisture uptake of flour fractions decreased with increased roasting time and temperature and this effect was shown to be significant with increased a_w, especially at high a_w levels. Flours stored in a_w's less

than 0.75 did not show mold growth throughout the storage period; however, mold mycelia were observed on the flour held under 0.92 and 0.97 a_w after one week.

Following two months storage, flours in a_w higher than 0.75 were moldy and discarded and the remaining samples from the optimum roasting process were further evaluated for quality change. HunterLab color values showed that although L values remained unchanged with increased a_w for all fractions, a_L and b_L values of these fractions increased with increased a_w indicating that flours became more red and more yellow toward higher a_w storage. Nitrogen solubility index (NSI) values decreased with increased storage a_w for all fractions except hull flour which had the lowest NSI values among fractions. Glucose level in the flours decreased significantly with increased a_w for all fractions. Significant reduction of starch content was found at 0.75 a_w for all fractions except hull flour. It was believed that increased a_w could result in increased browning reactions causing discoloration of flours with concurrent decrease of protein solubility and glucose levels. It was concluded that flours of all fractions stored at less than 0.75 a_w for two months at ambient temperature resulted in stable quality and suitability for food use.

Long term storage study indicated that flours stored up to 24 months with 6% and 9% moisture at 20°C or with 6% moisture at 37.7°C retained good quality.

Gelatinization and rheological properties of the purified navy bean starch pastes were evaluated with protocol developed using a computer-assisted Haake RV12 Rotovisco Viscometer. Aqueous starch pastes of four concentrations (6%, 8%, 10%, and 12%) were prepared in an MV cup with a perforated paddle mixer maintaining a constant rate of

shear of 50 rpm at temperatures of 75°C and 95°C for up to 60 min. Rotation of the paddle mixer at 50 rpm was shown to be the optimum speed for minimum mechanical breakdown of the pastes while providing homogeneous starch suspensions without starch precipitation at low concentrations and low temperatures. The activation energy of bean starch gelatinization could be readily estimated through this technique and was found to be 14.5 Kcal/g.mole.

Various swelling responses of navy bean starch during cooking were demonstrated. Maximum final viscosity values were obtained at 85°C for all starch concentrations except a maximum at 95°C for 6%. Thixotropic breakdown was observed for starch at 10% and 12% concentrations during initial shearing at high temperatures (85°C and 95°C) and this breakdown reached equilibrium after certain shearing time.

After the above cooking process, the flow behavior retrogradation tendency, and stability of the hot and cooled (50°C) pastes were determined. The power law, Herschel-Bulkley, and Casson models were employed to characterize the paste flow. The gelatinized pastes exhibited shear thinning behavior and their flow curves best fit the Herschel-Bulkley model over the range of shear rates tested. Yield stress, consistency index, and flow behavior index were generally concentration and temperature dependent. Significant changes of paste rheological properties occurred at starch concentrations above 10% for 75°C and above 8% to 10% for 85°C and 95°C.

RECOMMENDATIONS FOR FURTHER RESEARCH

1. It is suggested that the scanning electron microscope be employed to detect the status of the purified starch granules at various stages of the thermal response curves to further understand the mechanisms of granule swelling and breakdown in relationship to viscosity changes.

2. Studies could be conducted to evaluate the rheological properties of the purified navy bean starch paste after retort processing at various heating treatments.

3. Textural property studies of thermally produced navy bean starch gels using the Instron Universal Testing Machine should be conducted.

APPENDIX A

Table 17. Flow data of 6% navy bean starch paste cooked at 95°C for 60 min prior to measurements with the Haake Viscometer

Rep/ rpm		Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.553E-1	6.658E-4	4.374E+0	3.459E+0	0.55
	2	2.161E-1	9.625E-4	6.324E+0	4.921E+0	
	3	3.167E-1	1.099E-3	7.221E+0	7.388E+o	
	4	4.160E-1	1.332E-3	8.748E+0	9.643E+0	
	5	5.239E-1	1.471E-3	9.666E+0	1.269E+1	
	10	1.062E+0	1.819E-3	1.195E+1	2.486E+1	
	20	2.137E+0	3.001E-3	1.972E+1	4.960E+1	
	30	3.213E+0	3.534E-3	2.322E+1	7.623E+1	
	40	4.266E+0	4.048E-3	2.660E+1	1.009E+2	
	60	6.430E+0	4.832E-3	3.175E+0	1.549E+2	
	80	8.564E+0	5.317E-3	3.493E+1	2.083E+2	
	100	1.074E+1	5.787E-3	3.802E+1	2.595E+2	
2	1	1.407E-1	6.903E-4	4.545E+0	3.177E+0	0.58
	2	2.161E-1	9.915E-4	6.514E+0	4.973E+0	
	3	3.206E-1	1.164E-3	7.645E+0	7.572E+0	
	4	4.193E-1	1.336E-3	8.776E+0	9.897E+0	
	5	5.262E-1	1.467E-3	9.636E+0	1.256E+1	
	10	1.065E+0	1.967E-3	1.293E+1	2.541E+1	
	20	2.141E+0	2.641E-3	1.735E+1	5.109E+1	
	30	3.214E+0	3.106E-3	2.041E+1	7.628E+1	
	40	4.276E+0	3.560E-3	2.339E+1	1.019E+2	
	60	6.431E+0	4.351E-3	2.858E+1	1.509E+2	
	80	8.565E+0	4.962E-3	3.260E+1	1.992E+2	
	100	1.075E+1	5.518E-3	3.625E+1	2.553E+2	
3	1	1.499E-1	6.536E-4	4.294E+0	3.335E+0	0.64
	2	2.164E-1	9.984E-4	6.560E+0	4.913E+0	
	3	3.167E-1	1.153E-3	7.577E+0	7.564E+0	
	4	4.157E-1	1.302E-3	8.556E+0	9.832E+0	
	5	5.232E-1	1.448E-3	9.513E+0	1.236E+1	
	10	1.062E+0	1.997E-3	1.312E+1	2.525E+1	
	20	2.139E+0	2.703E-3	1.776E+1	5.051E+1	
	30	3.214E+0	3.258E-3	2.140E+1	7.582E+1	
	40	4.266E+0	3.726E-3	2.448E+1	1.023E+2	
	60	6.429E+0	4.415E-3	2.901E+1	1.519E+2	
	80	8.568E+0	4.958E-3	3.257E+1	2.013E+2	
	100	1.073E+1	5.472E-3	3.595E+1	2.649E+2	

APPENDIX B

Table 18. Flow data of 8% navy bean starch paste cooked at 95°C for 60 min prior to measurements with the Haake Viscometer

Rep/ rpm		Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.330E-1	1.446E-3	9.502E+0	3.033E+0	1.73
	2	2.164E-1	2.046E-3	1.344E+1	5.024E+0	
	3	3.201E-1	2.393E-3	1.572E+1	7.382E+0	
	4	4.182E-1	2.973E-3	1.953E+1	9.663E+0	
	5	5.266E-1	3.217E-3	2.114E+1	1.275E+1	
	10	1.065E+0	4.231E-3	2.870E+1	2.564E+1	
	20	2.140E+0	5.627E-3	3.697E+0	5.083E+1	
	30	3.213E+0	6.675E-3	4.386E+1	7.638E+1	
	40	4.271E+0	7.573E-3	4.975E+1	1.027E+2	
	60	6.426E+0	8.906E-3	5.852E+1	1.507E+2	
	80	8.562E+0	1.017E-2	6.681E+1	2.021E+2	
	100	1.075E+1	1.145E-2	7.519E+1	2.519E+2	
2	1	1.454E-1	1.479E-3	9.714E+0	3.253E+0	2.10
	2	2.165E-1	2.217E-3	1.456E+1	4.911E+0	
	3	3.105E-1	2.736E-3	1.797E+1	7.514E+0	
	4	4.190E-1	3.067E-3	2.015E+1	1.024E+1	
	5	5.262E-1	3.255E-3	2.139E+1	1.307E+1	
	10	1.064E+0	4.155E-3	2.730E+1	2.555E+1	
	20	2.140E+0	5.847E-3	3.841E+1	5.008E+1	
	30	3.213E+0	7.037E-3	4.623E+1	7.636E+1	
	40	4.274E+0	7.904E-3	5.193E+1	1.006E+2	
	60	6.428E+0	9.107E-3	5.983E+1	1.645E+2	
	80	8.563E+0	1.026E-0	6.740E+1	2.079E+2	
	100	1.075E+1	1.116E-2	7.332E+1	2.537E+2	
3	1	1.309E-1	1.590E-3	1.045E+1	3.101E+0	1.95
	2	2.159E-1	2.035E-3	1.344E+1	5.024E+0	
	3	3.182E-1	2.380E-3	1.572E+1	7.382E+0	
	4	4.199E-1	2.957E-3	1.953E+1	9.683E+0	
	5	5.280E-1	3.201E-3	2.114E+1	1.275E+1	
	10	1.063E+0	4.052E-3	2.662E+1	2.525E+1	
	20	2.139E+0	5.435E-3	3.571E+1	5.105E+1	
	30	3.213E+0	6.424E-3	4.220E+1	7.649E+1	
	40	4.270E+0	7.281E-3	4.784E+1	1.028E+2	
	60	6.427E+0	8.589E-3	5.643E+1	1.513E+2	
	80	8.564E+0	9.878E-3	6.490E+1	2.018E+2	
	100	1.075E+1	1.095E-2	7.192E+1	2.527E+2	

APPENDIX C

APPENDIX C

Table 19. Flow data of 10% navy bean starch paste cooked at 95°C for 60 min prior to measurements with the Haake Viscometer

Rep/ rpm		Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.457E-1	3.226E-3	2.120E+1	3.293E+0	6.80
	2	2.146E-1	4.442E-3	2.919E+1	4.952E+0	
	3	3.174E-1	5.141E-3	3.377E+1	7.760E+0	
	4	4.163E-1	5.587E-3	3.671E+1	1.013E+1	
	5	5.247E-1	6.126E-3	4.025E+1	1.260E+1	
	10	1.062E+0	8.066E-3	5.299E+1	2.550E+1	
	20	2.139E+0	1.076E-2	7.067E+1	5.075E+1	
	30	3.213E+0	1.291E-2	8.484E+1	7.614E+1	
	40	4.265E+0	1.463E-2	9.610E+1	1.006E+2	
	60	6.428E+0	1.795E-2	1.179E+2	1.505E+2	
	80	8.569E+0	2.081E-2	1.367E+2	2.010E+2	
	100	1.074E+1	2.338E-2	1.536E+2	2.492E+2	
2	1	1.475E-1	3.022E-3	1.986E+1	3.308E+0	6.61
	2	2.147E-1	4.336E-3	2.849E+1	4.933E+0	
	3	3.180E-1	4.905E-3	3.222E+1	7.668E+0	
	4	4.174E-1	5.536E-3	3.637E+1	9.960E+0	
	5	5.243E-1	6.048E-3	3.974E+1	1.260E+1	
	10	1.062E+0	7.987E-3	5.247E+1	2.545E+1	
	20	2.136E+0	1.065E-2	6.996E+1	5.070E+1	
	30	3.211E+0	1.282E-2	8.424E+1	7.584E+1	
	40	4.265E+0	1.463E-2	9.612E+1	1.004E+2	
	60	6.429E+0	1.786E-2	1.174E+2	1.506E+2	
	80	8.565E+0	2.071E-2	1.361E+2	2.002E+2	
	100	1.074E+1	2.329E-2	1.530E+2	2.506E+2	
3	1	1.871E-1	3.420E-3	2.247E+1	4.082E+0	6.70
	2	2.147E-1	4.650E-3	3.055E+1	4.754E+0	
	3	3.167E-1	5.389E-3	3.540E+1	7.714E+0	
	4	4.176E-1	5.887E-3	3.867E+1	1.029E+1	
	5	5.256E-1	6.341E-3	4.166E+1	1.279E+1	
	10	1.063E+0	8.298E-3	5.452E+1	2.556E+1	
	20	2.139E+0	1.103E-2	7.248E+1	5.094E+1	
	30	3.212E+0	1.310E-2	8.604E+1	7.638E+1	
	40	4.269E+0	1.484E-2	9.747E+1	1.008E+2	
	60	6.430E+0	1.810E-2	1.189E+2	1.505E+2	
	80	8.567E+0	2.099E-2	1.379E+2	2.006E+2	
	100	1.074E+1	2.362E-2	1.552E+2	2.498E+2	

APPENDIX D

APPENDIX D

Table 20. Flow data of 12% navy bean starch paste cooked at 95°C for 60 min prior to measurements with the Haake Viscometer

Rep/ rpm		Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.437E-1	6.359E-3	4.178E+1	3.254E+0	10.57
	2	2.147E-1	8.786E-3	5.772E+1	4.981E+0	
	3	3.170E-1	9.944E-3	6.533E+1	7.791E+0	
	4	4.174E-1	1.091E-2	7.167E+1	1.005E+1	
	5	5.252E-1	1.205E-2	7.916E+1	1.253E+1	
	10	1.063E+0	1.602E-2	1.053E+2	2.534E+1	
	20	2.137E+0	2.169E-2	1.425E+2	5.049E+1	
	30	3.207E+0	2.643E-2	1.737E+2	7.536E+1	
	40	4.256E+0	3.031E-2	1.991E+2	9.983E+1	
	60	6.424E+0	3.761E-2	2.471E+2	1.494E+2	
	80	8.566E+0	4.337E-2	2.849E+2	2.027E+2	
	100	1.075E+1	4.812E-2	3.162E+2	2.542E+2	
2	1	1.369E-1	6.515E-3	4.281E+1	3.108E+0	11.56
	2	2.155E-1	9.236E-3	6.068E+1	5.034E+0	
	3	3.164E-1	1.022E-2	6.717E+1	7.824E+0	
	4	4.180E-1	1.130E-2	7.427E+1	1.006E+1	
	5	5.256E-1	1.241E-2	8.156E+1	1.260E+1	
	10	1.063E+0	1.633E-2	1.073E+2	2.543E+1	
	20	2.138E+0	2.216E-2	1.456E+2	5.042E+1	
	30	3.207E+0	2.694E-2	1.770E+2	7.546E+1	
	40	4.256E+0	3.082E-2	2.025E+2	1.006E+2	
	60	6.426E+0	3.728E-2	2.450E+2	1.501E+2	
	80	8.569E+0	4.332E-2	2.846E+2	2.029E+2	
	100	1.075E+1	4.748E-2	3.119E+2	2.567E+2	
3	1	1.156E-1	6.736E+0	4.426E+1	2.724E+0	11.30
	2	2.172E-1	9.058E+0	5.951E+1	5.130E+0	
	3	3.193E-1	1.077E+1	7.077E+1	7.728E+0	
	4	4.212E-1	1.166E+1	7.661E+1	1.027E+1	
	5	5.290E-1	1.279E+1	8.404E+1	1.260E+1	
	10	1.065E+0	1.739E+1	1.143E+2	2.527E+1	
	20	2.139E+0	2.397E+1	1.575E+2	5.034E+1	
	30	3.211E+0	2.902E+1	1.906E+2	7.553E+1	
	40	4.266E+0	3.333E+1	2.190E+2	1.004E+2	
	60	6.426E+0	4.028E+1	2.646E+2	1.518E+2	
	80	8.566E+0	4.563E+1	2.998E+2	2.043E+2	
	100	1.075E+1	4.999E+1	3.284E+2	2.557E+2	

APPENDIX E

APPENDIX E

Table 21. Flow data of 6% navy bean starch paste cooked at 95°C for 60 min and cooled to 50°C prior to measurements with the Haake Viscometer

Rep/ rpm		Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.547E-1	9.755E-4	6.409E+0	3.436E+0	0.59
	2	2.156E-1	1.458E-3	9.577E+0	4.868E+o	
	3	3.170E-1	1.750E-3	1.150E+1	7.569E+0	
	4	4.152E-1	1.926E-3	1.265E+1	9.984E+0	
	5	5.236E-1	2.124E-3	1.396E+1	1.242E+1	
	10	1.061E+0	2.935E-3	1.928E+1	2.512E+1	
	20	2.136E+0	4.009E-3	2.634E+1	5.067E+1	
	30	3.213E+0	4.785E-3	3.144E+1	7.590E+1	
	40	4.265E+0	5.488E-3	3.606E+1	1.012E+2	
	60	6.428E+0	6.665E-3	4.379E+1	1.507E+2	
	80	8.561E+0	7.557E-3	4.965E+1	1.989E+2	
	100	1.073E+1	8.523E-3	5.600E+2	2.564E+2	
2	1	1.237E-1	1.135E-3	7.456E+0	2.822E+0	0.63
	2	2.156E-1	1.683E-3	1.106E+1	5.044E+0	
	3	3.178E-1	1.898E-3	1.247E+1	7.710E+0	
	4	4.163E-1	2.122E-3	1.394E+1	9.977E+0	
	5	5.237E-1	2.319E-3	1.523E+1	1.257E+1	
	10	1.061E+0	3.086E-3	2.028E+1	2.525E+1	
	20	2.136E+0	4.205E-3	2.763E+1	5.099E+1	
	30	3.213E+0	4.954E-3	3.255E+1	7.659E+1	
	40	4.263E+0	5.609E-3	3.685E+1	1.016E+2	
	60	6.427E+0	6.738E-3	4.427E+1	1.521E+2	
	80	8.561E+0	7.607E-3	4.998E+1	2.613E+2	
	100	1.073E+1	8.476E-3	5.569E+1	2.547E+2	
3	1	1.235E-1	1.148E-3	7.654E+0	2.895E+0	0.62
	2	2.158E-1	1.694E-3	1.108E+1	5.423E+0	
	3	3.179E-1	1.904E-3	1.345E+1	7.925E+0	
	4	4.184E-1	2.142E-3	1.406E+1	1.042E+1	
	5	5.270E-1	2.415E-3	1.542E+1	1.285E+1	
	10	1.064E+0	3.098E-3	2.098E+1	2.542E+1	
	20	2.140E+0	4.306E-3	2.875E+1	5.098E+1	
	30	3.250E+0	4.996E-3	3.524E+1	7.542E+1	
	40	4.452E+0	5.867E-3	3.965E+1	1.045E+2	
	60	6.435E+0	6.796E-3	4.473E+1	1.534E+2	
	80	8.904E+0	7.908E-3	5.004E+1	2.048E+2	
	100	1.080E+1	9.045E-3	5.692E+1	2.642E+2	

APPENDIX F

APPENDIX F

Table 22. Flow data of 8% navy bean starch paste cooked at 95°C for 60 min and cooled to 50°C prior to measurements with the Haake Viscometer

Rep/	rpm	Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.060E-1	3.264E-3	2.144E+1	2.484E+0	4.80
	2	2.138E-1	4.639E-3	3.048E+1	5.044E+0	
	3	3.161E-1	5.484E-3	3.603E+1	7.413E+0	
	4	4.161E-1	6.404E-3	4.207E+1	9.743E+0	
	5	5.252E-1	7.103E-3	4.667E+1	1.277E+1	
	10	1.061E+0	8.566E-3	5.628E+1	2.654E+1	
	20	2.137E+0	1.091E-2	7/167E+1	5.123E+1	
	30	3.211E+0	1.287E-2	8.457E+1	7.675E+1	
	40	4.256E+0	1.446E-2	9.502E+1	1.013E+2	
	60	6.419E+0	1.755E-2	1.153E+2	1.502E+2	
	80	8.571E+0	2.039E-2	1.340E+2	2.004E+2	
	100	1.072E+1	2.290E-2	1.505E+2	2.491E+2	
2	1	1.244E-1	3.384E-3	2.223E+1	2.341E+0	4.88
	2	2.139E-1	4.926E-3	3.237E+1	4.991E+0	
	3	3.160E-1	5.661E-3	3.719E+1	7.745E+0	
	4	4.165E-1	6.168E-3	4.052E+1	1.025E+1	
	5	5.249E-1	6.666E-3	4.379E+1	1.281E+1	
	10	1.062E+0	8.562E-3	5.625E+1	2.579E+1	
	20	2.138E+0	1.113E-2	7.314E+1	5.111E+1	
	30	3.212E+0	1.324E-2	8.697E+1	7.650E+1	
	40	4.264E+0	1.492E-2	9.802E+1	1.011E+2	
	60	6.429E+0	1.810E-2	1.189E+2	1.511E+2	
	80	8.568E+0	2.088E-2	1.372E+2	1.994E+2	
	100	1.076E+1	2.343E-2	1.539E+2	2.553E+2	
3	1	1.106E-1	3.339E-3	2.194E+1	2.587E+0	4.92
	2	2.140E-1	4.676E-3	3.072E+1	4.991E+0	
	3	3.174E-1	5.801E-3	3.811E+1	7.643E+0	
	4	4.159E-1	6.160E-3	4.047E+1	1.064E+1	
	5	5.241E-1	6.574E-3	4.319E+1	1.293E+1	
	10	1.063E+0	8.445E-3	5.548E+1	2.583E+1	
	20	2.138E+0	1.098E-3	7.217E+1	5.117E+1	
	30	3.212E+0	1.297E-3	8.521E+1	7.653E+1	
	40	4.261E+0	1.467E-3	9.636E+1	1.008E+2	
	60	6.425E+0	1.789E-3	1.176E+2	1.507E+2	
	80	8.570E+0	2.074E-3	1.362E+2	1.996E+2	
	100	1.076E+1	2.344E-3	1.546E+2	2.504E+2	

APPENDIX G

APPENDIX G

Table 23. Flow data of 10% navy bean starch paste cooked at 95°C for 60 min and cooled to 50°C prior to measurements with the Haake Viscometer

Rep/ rpm		Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.200E-1	6.238E-3	4.098E+1	2.761E+0	12.36
	2	2.138E-1	8.972E-3	5.894E+1	5.117E+0	
	3	3.161E-1	9.624E-3	6.323E+1	7.862E+0	
	4	4.163E-1	1.081E-2	7.102E+1	1.046E+1	
	5	5.241E-1	1.117E-2	7.335E+1	1.388E+1	
	10	1.061E+0	1.361E-2	8.940E+1	2.619E+1	
	20	2.136E+0	1.773E-2	1.165E+2	5.093E+1	
	30	3.207E+0	2.107E-2	1.384E+2	7.620E+1	
	40	4.261E+0	2.390E-2	1.570E+2	1.012E+2	
	60	6.424E+0	2.908E-2	1.910E+2	1.500E+2	
	80	8.562E+0	3.354E-2	2.204E+2	2.009E+2	
	100	1.074E+1	3.742E-2	2.458E+2	2.531E+2	
2	1	1.377E-1	6.649E-3	3.806E+1	3.112E+0	12.55
	2	2.149E-1	9.627E-3	5.352E+1	4.983E+0	
	3	3.170E-1	1.083E-2	5.943E+1	7.713E+0	
	4	4.165E-1	1.209E-2	6.542E+1	1.018E+1	
	5	5.254E-1	1.290E-2	6.905E+1	1.384E+1	
	10	1.062E+0	1.436E-2	8.718E+1	2.765E+1	
	20	2.135E+0	1.811E-2	1.190E+2	5.128E+1	
	30	3.211E+0	2.146E-2	1.410E+2	7.631E+1	
	40	4.264E+0	2.437E-2	1.601E+2	1.012E+2	
	60	6.427E+0	2.949E-2	1.937E+2	1.505E+2	
	80	8.563E+0	3.393E-2	2.229E+2	2.020E+2	
	100	1.074E+1	3.781E-2	2.484E+2	2.515E+2	
3	1	1.189E-1	5.347E-3	3.513E+1	2.770E+0	12.72
	2	2.142E-1	7.320E-3	4.809E+1	5.064E+0	
	3	3.155E-1	8.465E-3	5.562E+1	7.784E+0	
	4	4.174E-1	9.104E-3	5.981E+1	1.039E+1	
	5	5.253E-1	9.843E-3	6.467E+1	1/273E+1	
	10	1.063E+0	1.293E-2	8.496E+1	2.551E+1	
	20	2.135E+0	1.732E-2	1.138E+2	5.060E+1	
	30	3.211E+0	2.079E-2	1.366E+2	7/604E+1	
	40	4.262E+0	2.360E-2	1.551E+2	1.068E+2	
	60	6.426E+0	2/892E-2	1.900E+2	1.502E+2	
	80	8.560E+0	3.329E-2	2.187E+2	2.008E+2	
	100	1.074E+1	3.717E-2	2.442E+2	2.530E+2	

APPENDIX H

APPENDIX H

Table 24. Flow data of 12% navy bean starch paste cooked at 95°C for 60 min and cooled to 50°C prior to measurements with the Haake Viscometer

Rep/ rpm		Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.312E-1	1.065E-2	6.994E+1	3.017E+0	21.29
	2	2.155E-1	1.455E-2	9.561E+1	5.138E+0	
	3	3.157E-1	1.576E-2	1.035E+2	8.333E+0	
	4	4.177E-1	1.675E-2	1.101E+2	9.776E+0	
	5	5.260E-1	2.013E-2	1.322E+2	1.237E+1	
	10	1.062E+0	2.260E-2	1.485E+2	2.534E+1	
	15	1.595E+0	2.971E-2	1.952E+2	3.678E+1	
	20	2.136E+0	3.485E-2	2.290E+2	5.003E+1	
	30	3.207E+0	4.199E-2	2.759E+2	7.585E+1	
	40	4.255E+0	4.765E-2	3.131E+2	9.969E+1	
	50	5.348E+0	5.412E-2	3.555E+2	1.242E+2	
2	1	1.321E-1	1.193E-2	7.839E+1	2.990E+0	23.12
	2	2.160E-1	1.775E-2	1.166E+2	5.040E+0	
	3	3.156E-1	1.945E-2	1.278E+2	7.988E+0	
	4	4.188E-1	2.114E-2	1.389E+2	1.046E+1	
	5	5.273E-1	2.260E-2	1.485E+2	1.298E+1	
	10	1.064E+0	2.905E-2	1.908E+2	2.560E+1	
	15	1.594E+0	3.433E-2	2.255E+2	3.827E+1	
	20	2.136E+0	3.832E-2	2.518E+2	5.139E+1	
	30	3.206E+0	4.505E-2	2.960E+2	7.608E+1	
	40	4.251E+0	5.157E-2	3.388E+2	1.059E+2	
	50	5.156E+0	5.272E-2	3.464E+2	1.250E+2	
3	1	1.303E-1	1.045E-2	6.868E+1	3.006E+0	22.50
	2	2.166E-1	1.420E-2	9.329E+1	5.170E+0	
	3	3.140E-1	1.547E-2	1.016E+2	7.707E+0	
	4	4.198E-1	1.753E-2	1.152E+2	9.850E+0	
	5	5.277E-1	1.990E-2	1.308E+2	1.254E+1	
	10	1.063E+0	2.477E-2	1.628E+2	2.623E+1	
	15	1.594E+0	2.824E-2	1.855E+2	3.815E+1	
	20	2.136E+0	3.257E-2	2.140E+2	5.123E+1	
	30	3.207E+0	3.688E-2	2.423E+2	7.618E+1	
	40	4.252E+0	4.324E-2	2.841E+2	9.946E+1	
	50	5.349E+0	4.799E-2	3.153E+2	1.265E+2	

APPENDIX I

APPENDIX I

Table 25. Flow data of 6% navy bean starch paste cooked at 95°C for 60 min, cooled to 50°C, and held at 50°C for 30 min prior to measurements with the Haake Viscometer

Rep/ rpm		Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.083E-1	8.883E-4	5.836E+0	2.484E+0	0.67
	2	2.161E-1	1.391E-3	9.140E+0	5.040E+0	
	3	3.172E-1	1.627E-3	1.069E+1	7.614E+0	
	4	4.154E-1	1.803E-3	1.184E+1	9.938E+0	
	5	5.227E-1	1.991E-3	1.308E+1	1.246E+1	
	10	1.061E+0	2.664E-3	1.750E+1	2.524E+1	
	20	2.136E+0	3.688E-3	2.423E+1	5.027E+1	
	30	3.210E+0	4.448E-3	2.922E+1	7.582E+1	
	40	4.262E+0	5.064E-3	3.327E+1	1.015E+2	
	60	6.425E+0	6.097E-3	4.006E+1	1.505E+2	
	80	8.556E+0	7.014E-3	4.608E+1	2.026E+2	
	100	1.075E+1	7.874E-3	5.173E+1	2.471E+2	
2	1	1.289E-1	1.026E-3	6.739E+0	2.920E+0	0.63
	2	2.153E-1	1.548E-3	1.017E+1	4.996E+0	
	3	3.157E-1	1.749E-3	1.149E+1	7.625E+0	
	4	4.147E-1	1.967E-3	1.292E+1	9.897E+0	
	5	5.227E-1	2.158E-3	1.418E+1	1.250E+1	
	10	1.061E+0	2.897E-3	1.904E+1	2.545E+1	
	20	2.137E+0	3.862E-3	2.537E+1	5.071E+1	
	30	3.212E+0	4.591E-3	3.016E+1	7.656E+1	
	40	4.263E+0	5.166E-3	3.394E+1	1.018E+2	
	60	6.424E+0	6.281E-3	4.126E+1	1.510E+2	
	80	8.560E+0	7.145E-3	4.694E+1	1.995E+2	
	100	1.075E+1	8.017E-3	5.267E+1	2.551E+2	
3	1	1.075E-1	1.057E-3	6.943E+0	2.489E+0	0.66
	2	2.155E-1	1.576E-3	1.036E+1	5.088E+0	
	3	3.172E-1	1.802E-3	1.184E+1	7.595E+0	
	4	4.148E-1	2.039E-3	1.339E+1	9.845E+0	
	5	5.218E-1	2.243E-3	1.474E+1	1.255E+1	
	10	1.060E+0	2.893E-3	1.901E+1	2.554E+1	
	20	2.137E+0	3.909E-3	2.568E+1	5.060E+1	
	30	3.209E+0	4.665E-3	3.065E+1	7.630E+1	
	40	4.260E+0	5.264E-3	3.459E+1	1.020E+2	
	60	6.425E+0	6.331E-3	4.160E+1	1.514E+2	
	80	8.566E+0	7.264E-3	4.733E+1	1.991E+2	
	100	1.075E+1	8.087E-3	5.313E+1	2.568E+2	

APPENDIX J

Table 26. Flow data of 8% navy bean starch paste cooked at 95°C for 60 min, cooled to 50°C, and held at 50°C for 30 min prior to measurements with the Haake Viscometer

Rep/ rpm		Angular Velocity (Rad/sec)	Torque (N-m)	Shear Stress (N/m^2)	Shear Rate (1/sec)	Yield Stress (N/m^2)
1	1	1.206E-1	3.550E-3	2.332E+1	2.806E+0	4.93
	2	2.148E-1	4.852E-3	3.188E+1	5.253E+0	
	3	3.178E-1	5.121E-3	3.364E+1	7.897E+0	
	4	4.173E-1	5.816E-3	3.821E+1	9.582E+0	
	5	5.256E-1	7.029E-3	4.618E+1	1.217E+1	
	10	1.062E+0	8.887E-3	5.839E+1	2.539E+1	
	20	2.139E+0	1.204E-2	7.909E+1	5.132E+1	
	30	3.206E+0	1.432E-2	9.410E+1	7.828E+1	
	40	4.262E+0	1.541E-2	1.012E+2	1.102E+2	
	60	6.417E+0	1.727E-2	1.134E+2	1.532E+2	
	80	8.567E+0	1.977E-2	1.299E+2	2.031E+2	
	100	1.074E+1	2.214E-2	1.455E+2	2.486E+2	
2	1	1.547E-1	3.744E-3	2.460E+1	3.440E+0	4.85
	2	2.151E-1	5.517E-3	3.625E+1	4.670E+0	
	3	3.185E-1	6.526E-3	4.287E+1	7.681E+0	
	4	4.182E-1	7.141E-3	4.691E+1	1.046E+1	
	5	5.264E-1	7.558E-3	4.966E+1	1.326E+1	
	10	1.063E+0	9.372E-3	6.157E+1	2.625E+1	
	20	2.135E+0	1.183E-2	7.769E+1	5.184E+1	
	30	3.208E+0	1.377E-2	9.046E+1	7.711E+1	
	40	4.263E+0	1.545E-2	1.015E+2	1.017E+2	
	60	6.417E+0	1.846E-2	1.213E+2	1.517E+2	
	80	8.543E+0	2.105E-2	1.383E+2	2.005E+2	
	100	1.074E+1	2.360E-2	1.551E+2	2.532E+2	
3	1	1.386E-1	3.759E-3	2.470E+1	3.163E+0	4.89
	2	2.146E-1	5.119E-3	3.363E+1	4.952E+0	
	3	3.180E-1	6.219E-3	4.086E+1	7.533E+0	
	4	4.178E-1	6.932E-3	4.554E+1	1.029E+1	
	5	5.256E-1	7.335E-3	4.819E+1	1.310E+1	
	10	1.064E+0	9.369E-3	6.156E+1	2.612E+1	
	20	2.137E+0	1.174E-2	7.712E+1	5.202E+1	
	30	3.209E+0	1.361E-2	8.938E+1	7.734E+1	
	40	4.260E+0	1.523E-2	1.001E+2	1.018E+2	
	60	6.421E+0	1.824E-2	1.199E+2	1.517E+2	
	80	8.548E+0	2.085E-2	1.370E+2	2.014E+2	
	100	1.074E+1	2.331E-2	1.532E+2	2.511E+2	

APPENDIX K

APPENDIX K

Table 27. Analysis of variance of rheological parameters computed from selected flow models for navy bean starch pastes of various concentrations cooked at 75°C, 85°C, and 95°C for 60 min prior to measurements with the Haake Viscometer

Source of Variation	df	Power Law		Herschel-Bulkley[1]			Herschel-Bulkley[2]			Casson	
		K	n	τ_y	K	n	τ_o	K	n	K_o^2	K_c
						Mean Squares					
Treatment	11	407.527***	0.060***	75.143***	213.668***	0.042***	70.965***	337.149***	0.038***	680.350***	0.213***
Temp	2	578.579***	0.168***	117.882***	286.631***	0.121***	96.376***	528.867***	0.118***	954.252***	0.286***
Conc	3	845.467***	0.066***	147.356***	457.774***	0.040***	134.703***	704.337***	0.017***	1498.828***	0.558***
Temp X Conc	6	131.540***	0.022***	24.790***	67.258***	0.017***	30.626***	162.982***	0.021***	179.811***	0.016***
Error	24	0.201	0.001	0.127	0.153	0.001	0.006	0.115	0.001	0.509	0.001
Total	35	128.218	0.020	23.700	67.258	0.014	22.307	118.611	0.012	214.173	0.067
CV (%)		4.57	5.75	8.71	5.50	5.45	2.08	3.84	5.86	5.19	7.35

[1]With given yield stress (τ_y) from direct measurement

[2]Non-linear curve fitting

APPENDIX L

APPENDIX L

Table 28. Correlation coefficients, r^2, and sum-of-squares function, SS(b), for regression analysis of the flow curve data[1]

Treatment Temp,Conc (°C,% db)		r^2			SS(b)
		Power Law	Herschel-Bulkley	Casson	Herschel-Bulkley
75	6	0.9200	0.9045	0.8625	260.30
	8	0.9890	0.9890	0.9800	102.32
	10	0.9679	0.9666	0.9412	176.14
	12	0.9742	0.9632	0.9387	120.43
85	6	0.9822	0.9822	0.9617	54.72
	8	0.9910	0.9791	0.9639	51.98
	10	0.9933	0.9847	0.9779	182.32
	12	0.9922	0.9866	0.9775	200.25
95	6	0.9936	0.9915	0.9702	29.70
	8	0.9938	0.9891	0.9711	56.12
	10	0.9941	0.9912	0.9871	308.30
75/50	6	0.9520	0.9400	0.9195	240.25
	8	0.9847	0.9847	0.9620	201.38
	10	0.9734	0.9653	0.9388	176.42
	12	0.9711	0.9294	0.9054	200.45
85/50	6	0.9861	0.9861	0.9629	15.50
	8	0.9927	0.9709	0.9629	104.50
	10	0.9864	0.9760	0.9662	162.33
	12	0.9648	0.9563	0.9515	180.27
95/50	6	0.9963	0.9955	0.9785	13.17
	8	0.9945	0.9936	0.9851	168.86
	10	0.9919	0.9933	0.9896	417.88
	12	0.9859	0.9831	0.9810	204.50
75/50/50	6	0.9245	0.9232	0.9045	134.95
	8	0.9423	0.9328	0.9288	106.32
	10	0.9433	0.9405	0.9234	107.05
	12	0.9426	0.9401	0.9382	235.25

Table 28 (cont'd.)

Treatment Temp,Conc (°C, %db)	r^2			SS(b)
	Power Law	Herschel-Bulkley	Casson	Herschel-Bulkley
85/ 6	0.9213	0.9213	0.9179	160.98
50/ 8	0.9913	0.9762	0.9724	108.95
50				
95/ 6	0.9975	0.9969	0.9809	124.32
50/ 8	0.9894	0.9870	0.9748	177.45
50				

[1] n = 3

APPENDIX M

Table 29. Analysis of variance of rheological parameters computed from selected flow models for navy bean starch pastes of various concentrations cooked at 75°C, 85°C, and 95°C for 60 min and cooled to 50°C prior to measurements with the Haake Viscometer

Source of Variation	df	Power Law		Herschel-Bulkley[1]			Herschel-Bulkley[2]			Casson	
		K	n	τ_y	K	n	τ_o	K	n	K_o^2	K_c
		Mean Squares									
Treatment	11	1615.471***	0.063***	251.262***	831.997***	0.042***	205.938***	995.810	0.050***	1742.920	0.655***
Temp	2	2265.069***	0.217***	377.808***	1130.032***	0.161***	257.054***	1385.275	0.198***	2813.698	0.777***
Conc	3	3234.929***	0.045***	524.681***	1632.537***	0.019***	461.518***	1942.500	0.023***	3690.905	1.361***
Temp X Conc	6	589.210***	0.020***	72.371***	331.882***	0.013***	61.109***	392.644	0.014***	412.001	0.261***
Error	24	8.625	0.001	0.098	6.947	0.001	0.001***	0.297	0.001	20.247	0.002
Total	35	513.634	0.020	79.035	266.248	0.014	64.724	313.172	0.016	561.659	0.207
CV (%)		15.69	6.08	4.06	19.80	5.65	0.49	3.81	6.08	19.75	7.99

[1]With given yield stress from direct measurement

[2]Non-linear curve fitting

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