1 Introduction

1.1 Relevance of potato production in Germany

The potato (*Solanum tuberosum*) has been cultivated for several thousand years. The potato originated in highlands along the Andes Mountains from Peru to Bolivia, in South America (Burton, 1966) was introduced to Europe by Spanish explorers in the middle of the 16th century. Suitable climatic and soil conditions allowed the spread of the potato progressively on all continents, mostly in temperate regions and highland areas (Lisinska and Lezczynski, 1989).

The potato has become an important food crop in the world. The tuber as edible part of the potato plant is a staple food for many people, particularly in Europe and North and South America. World production in 2004 was more than 328 million tons, with China, Russia, India, USA and Ukraine being the five biggest potato producers. They account for more than 50% of world potato production (FAO-stat, 2004). Now the potato has become important as more than just a staple food. Food and non-food industries based on the potato are growing fast all over the world. The expansion of the utilizations of the potato has made the quality of the potato tuber of key importance.

Germany is the second biggest potato producer in Europe after Poland. Approximately 20% of the agricultural companies in Germany are working in potato production. In Germany, potatoes are the third most important crop after wheat and sugar beet, with a harvest area of 295,000 ha and a production rate of almost 13 Tg in 2004 (FAO-stat, 2004). From the total production, almost 25% is consumed directly as fresh or table potatoes and more than 42% goes to industry. More than 50% of the industrial potatoes are used in starch production. The second most important products are dried and frozen potatoes, which account for about 28% of the total for industrial potatoes (Schmitz and Wronka, 2002).

The Bundesverband der Deutschen Suesswarenindustrie (2004) in its annual report described potato chip production as important industries in the snack foods production. The potato chip production needs more than 5% of the German industrial potato output, or about 341,600 tons in 2001–2002. From that, about 100,500 tons potato chips were produced (Weber and Putz, 2003), which amounts to 234 million Euro a year. The Bundesverband der Deutschen Suesswarenindustrie (2004) calculated that the average per capita chip consumption in Germany accounts for about 880 g per person, or about 28% of total snack consumption. Compared to peanuts, cakes, and extruder products, potato chips become the most popular snack food for German people.

1.2 Factors affecting the quality of potato chips

For food products, appearance, taste, aroma, flavor, and texture, as well as nutrient value, are important quality parameters and become decision criteria for the food acceptance of consumers. The processing quality determines the quality of food products. On the processing line, potato slices are deep fried in oil at a temperature of 180–185°C. Water is removed from the slice and is replaced by oil amounting to as much as 35–40% of the finished chips (Bennett, 2001). A micro structural study of frying potatoes (Buchan and Aguilera, 2001) showed that water removal and volume alteration (shrinkage) of potato slices start at a temperature of 70–80°C, when the starch granules are completely gelatinized. Moreover, the oil is located mainly in the crust, while the core is virtually free from oil. The oil content of chips shows a negative relationship to the specific gravity of the potato tuber and to the thickness of the chip slice (Smith, 1987). When the temperature of the slice is near 150°C, the vacuole of the tuber cell begins to breakdown, sugars are released and the chip starts to develop color (Bennett, 2001). Costa et al. (2001) reported that crust formation starts when the potato surface reaches approximately 143°C. At a temperature of 180°C, potato chips show a crust-type structure only.

Bennett (2001) described the quality of potato chips as having a saddle-shape curl, being light gold in color, having no blemishes, being crisp and tender in the mouth, leaving a pleasant aftertaste, and having a slight potato flavor. From 30 volatile compounds of potato chips, pyrazine and aldehyde groups are reported to be the main compounds in the flavor formation of chips and their concentration in the potato chips depends on the fry oil used (Melton et al., 1993). Frying oil, as reported by Weber and Putz (2003), has an influence on the sensory acceptance of chips, which may be due to the fatty acid composition of the oil. However, the most difficult problem in the potato chip industry, according to Smith (1987), is the maintenance of a desirable color of chips throughout the year. Dark chips caused by the Maillard reaction are unattractive to the consumer and often have an undesirable flavor (Bennett, 2001).

The Maillard reaction is a non-enzymatic reaction between reducing sugars and amino acids which causes browning or darkening. The chemistry of the reaction is known to be a complex series of reactions leading to the formation of a variety of products, including flavors, aromas and colors. Color occurs due to the formation of high molecular weight (> 12,000 Daltons) polymeric compounds also known as melanoidins. These are generally formed by the reaction of the Amadori product or other dicarbonyls with amino acids (Fayle and Gerrard, 2002).

Chip darkening is described as a function of fry temperature and time, where lightness is decreased with increases in frying time and temperature (Sahin, 2000). The study of Roe et al. (1990) on chips from potatoes grown under different nitrogen regimes showed that the chip's color correlated to the total content of reducing sugars and free amino acids. The correlation is stronger than that from either reducing sugar or free amino acid alone. A study by Rodriguez-Saona et al. (1997) using artificial chips reported that the level of reducing sugars (D-glucose and D-fructose) and amino acids explained 75–88% of the color formation of chips, where an increase of 0.1 mg g^{-1} fresh

weight of reducing sugars causes a 1 unit decrease in mean L*–value and hue angle, while the amino acids asparagine and glutamine have only little effect on the chips' browning. Roe and Faulks (1991) reported that lysine, γ-amino-butyric acid and glycine were the main contributors to the browning of chips. Sucrose has also been reported to cause color formation, although the intensity is less than that caused by reducing sugars (Leszkowiat et al., 1990). During frying, sucrose may be hydrolyzed in the presence of glycine to yield glucose and fructose at temperatures as low as 150°C. Moreover, Rodriguez-Saona et al. (1997) suggested that ascorbic acid may also cause darkening, particularly when reducing sugars are at low concentration, but ascorbic acid concentration is usually not high enough to produce unacceptable darkening.

Asparagine and glutamine are known to be the major amino acids in potato tuber (Davies, 1977). The content of free asparagine and glutamine as well as glucose and fructose has been a more substantial quality parameter of chips since Swedish researcher in 2002 found acrylamide formation in a range of foods heated during production or preparation (Amrein, et al., 2003). Acrylamide is a toxic and carcinogenic compound for humans. It is established now that acrylamide can be formed during the frying of potato slices or pieces at temperatures of 120 to 150°C, accompanied by the Maillard reaction chain (Gertz and Klostermann, 2002).

1.3 Factors affecting the internal quality of potato tubers

Most research on chip's potato is focused on producing potatoes which have light chip color or a low content of reducing sugars. A carefully selection of varieties for chip production is important for processors. Some varieties for chips mainly grown in the USA are Kennebec, Chippewa, Russet Burbank, Katadhin, and Cherokee (Smith, 1987). In 2004, there were 41 varieties suitable for the chips processing in Germany and they were classified as very early, early, middle early and late varieties. The selection of varieties is based

on the content of dry matter and reducing sugars during storage, and sprouting problems (Putz, 2004).

Moreover, it was reported that several cultural factors such as drought and flood stress and nitrogen and potassium fertilization may have an effect on the color of potato chips. Drought stress during plant growth may have an influence on the maturity of the tuber, while immature tubers have high sugars content (Iritani, 1981; Schock et al., 1993). A pot experiment of Sulaiman (2000) with three potato varieties grown in water flood (100% water holding capacity = WHC) and water deficit (3% WHC) showed that growing potatoes in water flood led to an increase of D-glucose of 48–99% and D-fructose of 77–136%. On the contrary, potato growth in water deficit led to a decrease of D-glucose about 21–52% and D-fructose about 32–54%. After six months of storage at 4°C, the total reducing sugars content was kept lower in tubers grown under water deficiency than in tubers grown at sufficient water supply and water flood. Roe et al. (1990) reported about the effect of nitrogen fertilization on the increase of free amino acids and on the decrease of reducing sugars concentration in tubers, whilst the effect of storage on free amino acids in two varieties is described to be minor (Talley, et al. 1984). A study by Stanley and Jewell (1989) shows a trend of decreasing dry matter and total reducing sugars with an increasing rate of potassium fertilizer.

However, a wide range of investigations have focused on the behavior of the potato tuber in storage. It is already established that cold storage at 4–5°C causes sweetening of the tubers and reduce the color quality of chips (Coffin et al., 1987; Brown et al., 1990; Edwards et al., 2002). Cottrell et al. (1993) reported that the increasing of reducing sugars during cold storage is related to a remarkable increase in the activity of starch hydrolyzing enzymes such as α-amylase, β-amylase, and debranching enzyme during the first week of storage. The activity of these enzymes is reported to increase only slightly if the tuber is stored at a high temperature (10–11°C). Ross and Davies (1987) suggested

that α-amylase is responsible for the initiation of starch granule degradation, while β-amylase activity is high in unsprouted tubers, prior to the onset of rapid starch depletion. On the other hand, Sowokinos (2001) described the role of phosphorolytic enzymes in starch degradation. He suggested that starch conversion at a low temperature is following more the hexogenesis pathway (formation of glucose and fructose from sucrose) than the respiration pathway. The hexogenesis pathway is controlled by the enzymes UDP-glucose pyrophosphorylase, sucrose-6-phosphate synthase, and acid invertase in the cytoplasm and vacuole. In the respiration pathway, where the rate declines at a low temperature and *vice versa*, sugars are converted completely to CO_2, water, and energy. Moreover, varieties that resist sweetening in the cold have shown a higher rate of respiration in storage. However, there are some advantages to cold storage because it can prolong storage time, reduce the respiration rate and water loss, and inhibit sprouting (Van Es and Hartmans, 1981).

Copp et al. (2000) reported that in most cases the point at which increasing respiration rates during storage are observed to correspond to the point at which chip color quality starts to decline, although they did not get any correlation with the tubers' sugars content. They concluded also that an increase in the respiration rate is not always associated with the end of dormancy and sprouting, as had been concluded from previous studies.

Mechanical stress during harvest, handling, transportation and storage may cause an increase in reducing sugars accumulation during storage due to increasing invertase activity as reported by Hironaka et al. (2001). However, research related to mechanical stress is more focused on blackspot discoloration inside the tuber. Blackspot is a type of enzymatic discoloration as the result of oxidation of phenolic amino acids such as tyrosine by polyphenol oxidase. Deficiency of potassium increases the potential for blackspot formation in the tuber due to increasing of the free tyrosine in the tubers (McNabnay, et al., 1999). In contrast, blackspot potential is decreased for the water-stressed tuber from a potato grown in a pot (Pawelzik and Delgado, 1999). Further-

more, the study of Delgado et al. (2001) concluded that chlorogenic acid may contribute to blackspot formation in the tuber grown under water stress. For the chip industry, blackspot causes obvious quality deterioration and great losses. However, mechanical stress may be reduced through strengthening the outside of potato tubers; the increasing of the tuber Ca may be promising.

1.4 The importance of calcium for the plant and plant cell

Calcium in potato tuber tissue, according to the study of Davies and Millard (1985), can be divided into physiologically active and inactive forms. Physiologically active Ca occurs as free ion and as the water soluble Ca salts of organic acids, chlorides and nitrates and may be reversible bound to proteins and pectin. Calcium bound to phosphate, oxalate, carbonate and silicate salts exist in an inactive form. Davies and Millard (1985) found that more than 90% of tuber Ca is in a physiologically active form and very little is in the insoluble inactive form, such as Ca oxalate. Calcium oxalate and phosphate and water soluble Ca salts are mostly present in the vacuole (Marschner, 1995). Most of the Ca is a cell wall substance and is located in the appoplast, in the middle lamella and at the outside surface of the plasma membrane. In the middle lamella, Ca is bound to polygalacturonic acids in the pectin as Ca pectate. Calcium in small concentrations is present in the matrices of mitochondria and on plastid envelopes, in the vicinity of amyloplast, in plastids and in the endoplasmic reticulum, but not found within amyloplast (Oparka and Davies, 1988; White and Broadley, 2003). In the potato tuber, the concentration of Ca in the outer tissues (periderm and in the vascular ring) is approximately 400% higher than in the inner tissues (pith) (Oparka and Davies, 1988).

Calcium in a physiologically active form has been known to take part in the activities of many enzymes in the plant cell. Lopez-Nicolas et al. (2000) reported an increase of lipoxygenase activity in potato tubers in the presence of Ca^{2+}. Moreover, Marschner (1995) listed a number of enzymes that are activated by Ca^{2+}, i.e. α-amylase, phospholipase, ATPases, hexodiphosphatase

and PEP carboxylase. High Ca content in plant cells is also known to activate the pentose phosphate pathway and the biosynthesis of amino acids (Allan and Trewavas, 1987). A study of Wei and Sung (1993) on rice cultivated in solution with Ca supplement showed that carbohydrate metabolism enzymes such as sucrose synthase and invertase are induced by long-term Ca application. Furthermore, recent research showed that Ca stress (deficiency and excess of Ca) in *Mentha pulegium* L. leaves induced antioxidant enzymes and lipoxygenase activity, and furthermore Ca might take part in the senescence processes (Candan and Tarhan, 2005).

Calcium as a cell wall substance has a function in cell wall and membrane stabilization, and therefore it has an influence on tissue firmness and resistance against environmental stresses, microbial and nematode diseases. Many investigations reported the improvement of tissue integrity and firmness for pears, melons, apples, pineapples, as well as potatoes by the spraying of Ca directly on the skin surface or immersion of the fruits in the Ca solution (e.g. Gerasopoulos, 1999; Lester, 1999; Roy, 1999; Ahrne et al., 2003). It has been reported that Ca application may increase the pectin content in the cell wall and therefore increase the resistance of the potato tuber to nematodes and *Erwinia carotovora* (Fatemy and Evans, 1986; McGuire and Kelman, 1986). Calcium has been also reported to improve the resistance of the potato tuber to heat stress, while Ca deficiency led to internal disorders in potatoes, bitter pit in apples, and some physiological disorder in many fruits and vegetables (Kleinhenz and Palta, 2002; Sterrett and Henninger, 1991; Davies, 1998; Yuri et al., 2002).

Moreover, it was reported that Ca may delay the ripening of pears and as well as membrane lipid catabolism in apples during storage (Gerasopoulos, 1999; Picchioni et al., 1998) because Ca decreases the respiration rate and ethylene production (Recasens et al., 2004).

Recent research on the function of plant Ca is focused on the mechanism and the transport of Ca^{2+} in the cell as a second messenger if a plant is

under stress. The Ca concentration in the cytosol in plant cells is an indicator for environmental challenges, such as cold shock, salt, or mechanical stress. The concentration of Ca in the cytosol is very low, ranging between 0.1–1 µM (White and Broadley, 2003). Efflux or influx of Ca^{2+} from or to the cytosol occurs through different Ca^{2+}-channels from or to the appoplast, endoplasmic reticulum, vacuole or mitochondria and is regulated by Ca^{2+}-ATPases and H^{+}/Ca^{2+} antiporters. Some Ca-binding proteins such as calmodulin, calcineurin B-like proteins, Ca-dependent protein kinase, and some other Ca-binding proteins have also been implicated in cellular responses to diverse environmental, developmental and pathological challenges.

However, investigations on the effect of Ca on the quality of potato tubers were more focused on improving resistance against diseases and less to the chemical and biochemical attributes of tubers. Concerning the role of Ca^{2+} in respiration, carbohydrate metabolism enzymes, biosynthesis of amino acids, and firmness of plant tissue, Ca application on the potato plant may influence tuber quality, long-term storage stability of tubers, and certainly chips and starch quality.

1.5 Calcium fertilizer and calcium uptake of potato tuber

Calcium is classified as a macronutrient. Its availability in common soil is high and therefore Ca deficiency is rare in nature but may occur in soils with low base saturation or high level of acidic deposition (McLaughlin and Wimmer, 1999). The Ca concentration in a soil solution may reach 25 mmol L^{-1} but in average 1.25–2.5 mmol L^{-1}, or about ten times higher than potassium (Barber, 1985). However, Ca concentration in the tuber is very low compared to other macronutrients and sometimes Ca deficiency may occur. The content of Ca in the tuber falls in a wide range, between 75 and 3,060 mg kg^{-1} DM (Bamberg et al., 1998). The immobility of Ca in the phloem is the reason for the low Ca content of tubers. Calcium taken up from the soil is transported to leaves via xylem but cannot be re-translocated to the tuber (Krauss and Marschner,