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UNIVERSITAT POLITÈCNICA DE CATALUNYA

BARCELONATECH (UPC)

Agri-Food Engineering and Biotechnology

DOCTORAL THESIS

**Study of the effect of cooking methods on
physical properties and bioactive
compounds of selected potato cultivars
(*Solanum tuberosum L.*)**

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Chapter 1

Introduction

1.1 State of the art

The potato (*solanum tuberosum L.*) appeared in Europe during the last quarter of the sixteenth century, and potatoes are a main component of meals in many European countries (Murniece et al., 2011). In the developing countries, the poorest and undernourished families depend on potatoes as a major source of food and nutrition because of its highly available dietary energy. Potato is a carbohydrate-rich, versatile vegetable prepared and served in variety of ways worldwide. Despite of its nutritional quality and low production costs, the consumption of fresh potato is decreasing because of some quality issues. Mainly, potato cultivars are not use properly in terms of industry processing or culinary methods. It involves lower quality potato products or dishes. Sensorial texture is the key factor in the acceptance of potato and it depends on the changes of starch structure during the cooking method apart from the difference between cultivars and storage condition of the tubers (Poberezny, 2010; Seefeldt et al., 2011). But there are some other quality problems, as after-cooking darkness of potato, and the effect of cooking method in the bioactive compounds of potato that affect the quality of the potato products and are not as widely studied. Traditionally, there are three popular methods to cook the potatoes: boiling, deep-frying and baking. But only a few studies determine the aptitude of the potato cultivars on being processed depending on their composition and considering the new techniques.

1.2 Potato cultivars

The potatoes worldwide belong to just one biological species, *Solanum tuberosum L.*, but there are more than 4000 varieties of potatoes cultivated around the world with different colors, shapes, sizes, taste and texture characteristics. These cultivars are classified into four major groups: Russets, Reds, Yellows and Specialty (Anonymous, 2011). Russtes are characterized by even, oval shape, brown net-textured skin, shallow eyes with flesh color varying from creamy white to light golden. Red potatoes are characterized by a rozy skin

and a white flesh with a texture that is firm, smooth and moist. Yellows include Yukon Gold, which is always used by the cooking cultivar. Specialty cultivars include colored cultivars and fingerlings. Commercial potatoes consumed in Spain are normally stored potatoes. The primary potato cultivar is Monalisa (26%) followed by Agata (16%), Kennebec (16%), Caesar (8%), Agria (4%) and Red Pontiac (3%); the potato consumption rate in 2010 was 23.13 kg·person⁻¹·year⁻¹ (Ministerio de Agricultura Alimentación y Medio Ambiente, 2010).

1.3 Physiochemical properties

The potato tuber is a rich source of nutrients and energy. It is a good source of carbohydrates, proteins, vitamins, minerals, fiber, and antioxidants (Andre et al., 2007). The major carbohydrate in the potato tubers is starch, which contributes about 65-80% of the dry weight of the tubers (Cutter, 1992). Other important tuber carbohydrates include the sugars and dietary fiber. The sugar content may vary from only amounts to as much as 10% of the dry weight (Lisinska & Leszczynski, 1989). Furthermore, bioactive compounds as secondary plant metabolites found in the potato and other plants have been the subject of interest for the researchers because of their health-modulators. The phenolic compounds, as one of the most bioactive compounds present in the potato, are beneficial for the human diet. Table 1.1 shows the general compositions of potato tubers (Lisinska & Leszczynski, 1989).

Table 1.1 Chemical composition of potato tubers

Substance	Content (%)	
	Range	Mean
Dry matter	13.1-36.8	23.7
Starch	8.0-29.4	17.5
Reducing sugars	0.0-5.0	0.3
Total sugar	0.05-8.0	0.5
Crude fiber	0.17-3.48	0.71
Pectic substances	0.2-1.5	-
Total nitrogen	0.11-0.74	0.32
Crude protein (total nitrogen \times 6.25)	0.69-4.63	2.00
Protein nitrogen in total nitrogen	27.3-73.4	54.7
Amide nitrogen	0.029-0.052	-
Amino acid nitrogen	0.065-0.098	-
Nitrates	0.0-0.05	-
Lipids	0.02-0.2	0.12
Ash	0.44-1.87	1.10
Organic acids	0.4-1.0	0.6
Ascorbic acid and dehydroascorbic acid*	1.0-54.0	10.0-25.0
Glycoalkaloids*	0.2-41.0	3.0-10.0
Phenolic compounds*	5.0-30.0	-

*In mg/100 gfw

(Lisinska & Leszczynski, 1989)

1.3.1 Carbohydrates

Starch is a major product of many economically important crops, such as wheat, rice, maize, tapioca, and potato. Starch content varies with cultivar and plant growth stage (Agrawal et al., 2005; Li et al., 2006). The starch contributes to the texture, consistency and organoleptic qualities of the prepared food (Tharanathan, & Tharanathan, 2001). Starch is generally classified into rapidly digestible starch, slowly digestible starch and resistant

starch (RS), according to the rate and extent of its digestion (Song et al., 2010). The resistant starch is a form of starch or fractions of starch that is not hydrolyzed by enzymes in human digestive system (Haralampu, 2000) because of its crystalline nature and the ratio of amylose and amylopectin (Englyst et al., 1992). RS is in its own right valuable as a form of prebiotic carbohydrate fiber that may protect against cancer of the colon (Bird & Topping, 2001). Methods of food processing and cultivar affect the glycemic index of potatoes. The starch granules in potatoes were broken during cooking facilitating hydrolysis by pancreatic α -amylase, which consequently increases the glycemic index of cooked potatoes (Odenigbo et al., 2012). In addition, the resistant starch value of processed potato is lower compared to the resistant starch content in raw potato.

The sugars in potatoes are majority in the form of reducing monosaccharides such as D-glucose and D-fructose and non reducing disaccharides such as sucrose. The sugar content of potato varies with cultivars, storage and processing conditions. The sugar content is different depending on the part of the potato tuber (bud-end, stem-end and cortex). Weaver et al. (1978) reported that the higher amount of reducing sugars was in the cortex than bud-end and stem-end; however, the sucrose content was uniform throughout. The low temperature (0-6 °C) generally increases the sweetness of potatoes. In addition, Kumar et al. (2004) reported that the tubers stored at 8-12 °C had lower sugar concentration than that stored at 4-6 °C and the potatoes are generally stored at 8-12 °C (Takada et al., 2005). Sugars in foods play multifunctional roles, such as wetness, flavor, texture, etc. The reaction of a carbonyl group of reducing sugars (glucose and fructose) with the amino acids present in the potato tubers resulting in the browning reaction (Maillard reaction) with special flavor compounds (Pedreschi et al., 2009).

1.3.2 Phenolic compounds

The phenolic compounds represent a large group of minor plant products, which play an important role in determining the organoleptic properties of many kinds of fruits and

vegetables. The potatoes are also good source of phenolics (Brown, 2005). In the potato tubers, the phenolic compounds are mainly located in the potato peel and adhesive tissue cortex, and the content of phenolics decrease towards the center of the tuber (Weshahy & Rao, 2009). The phenolic compounds may degrade during extraction and storage conditions. In addition, the phenolic compounds may hydrolysis when exposed to high temperature, light and different storage conditions. Chlorogenic acid and caffeic acid are two of the most prominent phenolic acids reported in the potato tubers followed by protocatechuic acid, trans-cinnamic acid, para-coumaric acid, ferulic acid, vanillic acid, gallic acid, syringic acid and salicylic acid (Shakya & Navarre, 2006).

Potato peel is often wasted as the by-product of the potato processing industry. However, it is well know that they are rich in phenolics. Singh & Rajini (2008) analyzed the phenolic content in potato peel and it was found to offer significant protection to human erythrocyte membrane proteins from oxidative damage induced by ferrous-ascorbate. Current researches are primarily focused on phenolic compounds, responsible for antioxidant activity (Kaur, & Kapoor, 2002). Besides their antioxidant activity, the compounds also attracted great interests of scientists due to their health protecting properties. Therapeutic effects such as antibacterial, anti-inflammatory, antiallergic, antimutagenic, antiviral, antineoplastic, antithrombotic, and vasodilatory activity have been attributed to phenolic compounds (Deuber et al., 2012).

1.3.3 Physical properties

Color is one of the main qualities of fresh potatoes commonly used as selection criterion by the consumers and the fresh-cut industry, as well as an indicator of the overall quality and maturity stage of the product. Color varies among potatoes can be affected by cultivars and pre-harvest factors such as plant nutrition, seasonality, climate conditions, temperature, relative humidity, storage time, and postharvest handling conditions.

For all color parameters, the extent of color change in cooked potatoes was dependent on the

length of storage and storage temperature, higher temperatures and longer storage time resulting in larger changes (Nourian et al., 2003). Texture is generally described as a multi-parameter attribute, usually associated with mechanical, geometrical and acoustic parameters (Szczesniak, 1987). A recommended assay to study the texture of potato tubers is the textural analysis, including the textural profile analysis (TPA) and shear force, The instrumental tests used to measure the texture of solid foods, maybe perfectly valid for semisolid food products, with the advantage that they provide a rapid way of ascertaining and characterizing product texture (Canet et al., 2005). The texture of the raw potatoes is determined by several mutually dependent factors like cultivars, the agronomic, storage conditions, etc. Changes in texture that occur during processing result from changes in the chemistry of cell wall and middle lamella hydrophilic polymer material that affect the physical properties. However, the starch is the major component of the dry matter in potato cultivars. It can be assumed that the phenomena associated with gelatinization are involved in the texture changes during processing (Alvarez et al., 2001). In addition, Potatoes rich in dry matter can exhibit hard texture, whereas potatoes low in dry matter are characterized by greasy and sticky textures (Kita, 2002).

1.4 Effect of the cooking methods on potato properties

The consumption of fresh potato is decreasing because of some quality issues. Mainly, potato cultivars are not use properly in terms of industry processing or culinary methods. It included lower quality potato products or dishes, after-cooking darkness of potato, and the effect of cooking method in the bioactive compounds of potato that affect the cooked potato products and are not as widely studied. Traditionally, there are three popular methods to cook the potatoes: boiling, baking and frying. Nowadays, microwave is becoming also common method to cook them, but only a few studies determine the aptitude of the potato cultivars on being processed depending on their composition.

Boiling

Boiling reduced or, in some cases, enhanced the physiochemical compounds content of potato genotypes with respect to uncooked samples. As the Table 1.2 showed, different boiling conditions have significantly effect on the properties of potato tubers. From these research works, we can know that the shorter boiling time increased or did not change the total phenolic content, the antioxidant activity and the chlorogenic acid content (Navarre et al., 2010; Perla et al., 2012; Blessington et al., 2010; Lachman et al., 2013; Dao & Friedman, 1992; Mulinacci et al., 2008). The conflict of TPC after heat-treatments was due to the genotype of each cultivar and cooking conditions. The heat treatments may inactivate polyphenol oxidases preventing oxidation and polymerization of polyphenols, and the treatments could promote the release of dietary fiber-bound polyphenols forming the free phenolic compounds (Palermo et al., 2014). The reducing of TPC after cooking treatments was attributed to water-soluble phenolics leaching into the water (boiling) and the breakdown of the phenolics (Palermo et al., 2014). The boiling methods also led to the loss of the total starch and resistant starch of potato samples (Mulinacci et al., 2008). The texture of cooked potatoes depends on the cooking conditions as a result of various factors such as starch gelatinization, pectin degradation, cell wall breakdown, cell separation, etc. (Nourian et al., 2003). The textural properties were directly affected by cooking temperature/time conditions. As expected, cooked samples showed lower values compared with raw potatoes (Alvarez & Canet, 1998) and the softening of the potato tissues were remarkable different between cultivars (Alvarez et al., 2001), but when at 70 and 80 °C showed qualitatively similar softening curves. In addition, after being cooked, L* values decreased significantly which means that the potato samples get darker (Nourian et al., 2003).

Introduction

Table 1.2 Effect of boiling processing condition on nutritional compositions of potatoes

Physiochemical composition	Processing conditions		Conclusions	Reference
	Time			
Total phenolics (TP)	18 min		increased 71.3% of the amount of TP	Navarre et al., 2010
	60 min		42.9% loss of the total phenolics	Perla et al., 2012
Antioxidant activity (AC)	60 min		decreased 38.74% of the amount of the original AC (DPPH radical scavenging assay)	Perla et al., 2012
	25 min		increased the amount AC compared to uncooked potatoes	Blessington et al., 2010
	18 min		increased 14.98% of the amount of AC	Navarre et al., 2010
Chlorogenic acid	18 min		increased 32.8% of the content compared to uncooked potatoes	Navarre et al., 2010
	15 min		decreased to 52% of the original amount	Lachman et al., 2013
	30 min		60% loss of their original chlorogenic acid content	Dao, & Friedman, 1992
	20 min		did not change the chlorogenic acid content of potatoes	Mulinacci et al., 2008
Total anthocyanin content (TAC)	15 min		increased TAC 4.2 times compared to uncooked potato tubers	Lachman et al., 2012
	10 min		decreased by nearly half compared with the raw potato (using boiling-steamed method at 121°C)	Kim et al., 2012

Table 1.2 (Continued)			
Physiochemical composition	Processing conditions	Conclusions	Reference
	Time		
Total anthocyanin content (TAC)	15 min	increased 3.79 times of the original amount TAC	Lachman et al. 2013
	20 min	significantly decreased the anthocyanin content of the colored cultivars.	Mulinacci et al., 2008
Total starch	20 min	14.72-21.89% loss compared to uncooked potatoes	Mulinacci et al., 2008
Resistant starch	20 min	1.76-4.18% loss compared to uncooked potatoes	Mulinacci et al., 2008
Texture	15 min	The shear force was 945.6 N and 82.02 N, respectively for the fresh and cooked cylindrical potato samples.	Alvarez & Canet, 1998
	120 min	The softening curves obtained for each of the mechanical testes performed in a range of temperature studied, and found that at 70 and 80 °C showed qualitatively similar softening curves.	Alvarez et al., 2001
Color	10 min	A steady decrease in L* value of cooked cylindrical pieces of potatoes, demonstrating a progressive loss in brightness. The total color difference, ΔE , increased and the changes were clearly temperature dependent.	Nourian et al., 2003

Baking

Baking is a complex process which involves many physical, chemical and biochemical changes in food. In particular, during potatoes baking the starch gelatinization occurs including palatability, digestibility and softening to the raw starch matrix, and the heat is transferred into the potato tubers mainly by convection from the heating media (Barba et al., 2008). From the Table 1.3, we can know that there was lots of discrepancy about physiochemical compounds of potato samples, which could be due to the different processing conditions. Garcia-Alonso & Goni (2000) stated that the average content of total starch slightly decreased by boiling and baking in potato cultivars compared with the original value of raw potatoes and the baking potato samples had lower total starch values than boiled ones, which may be due to the gelatinization during baking and microwaving was more than boiling. It also found that the RS content retention of the baking was higher than the retention of the boiling in all tested cultivars, and the amount of RS depends on the degree of gelatinization and retrogradation during cooling of the potato products. The lower temperature and shorter time increased the bioactive compounds content (phenolics, chlorogenic acid, antioxidant activity, and anthocyanin) of potato samples (Perla et al., 2012; Navarre et al., 2010; Blessington et al., 2010; Lachman et al., 2013; Dao, & Friedman, 1992; Im et al., 2008; Lachman et al., 2012; Kim et al., 2012). Therefore, the baking temperature and time are very important for this method. However, no reference was found to evaluate the effect of baking conditions on the physical properties of potatoes.

Table 1.3 Effect of baking processing condition on nutritional compositions of potatoes

Physiochemical composition	Processing conditions		Conclusions	Reference
	Temperature	Time		
Total phenolics (TP)	204 °C	60 min	54.0% loss of the total phenolics	Perla et al., 2012
	375 °C	30 min	increased 120% of the amount of extractable phenolics	Navarre et al., 2010
Antioxidant activity (AC)	204 °C	60 min	decreased 57.13% of the amount of the original AC (DPPH radical scavenging assay)	Perla et al., 2012
	204 °C	15 min	increased the AC compared to uncooked potatoes	Blessington et al., 2010
	375 °C	30 min	increased 29.97% of the amount of AC	Navarre et al., 2010
Chlorogenic acid	375 °C	30 min	increased 24.6% of the original chlorogenic acid content	Navarre et al., 2010
	180 °C	45 min	decreased to 37% compared to the raw potatoes	Lachman et al., 2013
	212 °C	45 min	contained 0% of the original amount of chlorogenic acid	Dao, & Friedman, 1992
	200 °C	10 min	contained 90% to 100% of the chlorogenic acid and its isomer	Im et al., 2008

Table 1.3 (Continued)

Physiochemical composition	Processing conditions		Conclusions	Reference
	Temperature	Time		
Total anthocyanin content (TAC)	180 °C	40 min	increased TAC 3.34 times compared to the uncooked potatoes	Lachman et al., 2012
	200 °C	40-50 min	decreased 19.07% of TAC	Kim et al., 2012
	180 °C	45 min	increased 2.94 times of TAC	Lachman et al., 2013
Total starch	200 °C	50 min	decreased to 65.91% of potato samples (79.36% of the fresh potatoes)	Garcia-Alonso & Goni, 2000
Resistant starch	200 °C	50 min	decreased significantly to 3.7% of potato samples (69.05% of fresh potatoes)	Garcia-Alonso & Goni, 2000

Microwaving

In recent years, many researches focused on studying the treatments to obtain the products which keep the majority of their original properties. The best potato processing treatments should be low loss of volatiles, flavors, color, texture, and nutritional compounds. Actually, there are lots of benefits in microwave processing for potato tubers, such as reductions in manufacturing costs due to energy saving and shorter processing times, improving product uniformity and yields (Barba et al., 2008). Blessington et al. (2010) reported that boiling resulted in significantly lower antioxidant activity and total phenolics content, as compared to baking, frying and microwaving. Baking, frying, and microwaving also increased the levels of chlorogenic acid, caffeic acid, (-) epicatechin, p-coumaric acid and vanillic acid, but decreased quercetin dehydrate when compared to uncooked potato samples. In recent years, there are some research works on the effect of microwaving on potato physiochemical properties. However, similar with other cooking methods, the results of their studies were conflicted (Table 1.4).

The microwaving performed at 500 W reduced the phenolic content. This reduction was significantly lower than other different power levels (Barba et al., 2008). The shorter microwaving time increased the antioxidant activity and chlorogenic acid content (Blessington et al., 2010; Navarre et al., 2010; Dao, & Friedman, 1992). The microwaving methods led to the loss of the total starch and resistant starch (Mulinacci et al., 2008). However, the results about the effect of microwaving on the total anthocyanin content were also conflicted (Lachman et al., 2012; Lachman et al., 2013; Mulinacci et al., 2008), which may also be due to the different potato cultivars. Until now, still no reference introduce the changing of physical properties (color and texture).

Table 1.4 Effect of microwaving processing condition on nutritional compositions of potatoes.

Physiochemical composition	Processing conditions		Conclusions	Reference
	Power (w)	Time		
Total phenolics (TP)	1100W	2.5min	increased 31.1% of the amount of the original TP content	Navarre et al., 2010
	-	10min	decreased 51.1% of the TP original content	Perla et al., 2012
	750W	2min	32.10% loss of TP content	Barba et al., 2008
	500W	2min	3.99% loss of TP content	Barba et al., 2008
	300W	2min	26.53% loss of TP content	Barba et al., 2008
Antioxidant acitivity (AC)	-	10min	decreased 48.58% of the AC amount (DPPH radical scavenging assay)	Perla et al., 2012
	800W	2.5min	increased 68.18% of the AC amount compared to uncooked potatoes	Blessington et al., 2010
	1100W	2.5min	increased 29.97% of the amount of the original AC content	Navarre et al., 2010
Chlorogenic acid	-	2.5min	increased 41.0% of the chlorogenic acid content	Navarre et al., 2010
	750W	10min	decreased to 28% of the original chlorogenic acid content	Lachman et al., 2013
	-	30min	45% loss of the chlorogenic acid content of potatoes.	Dao, & Friedman, 1992
Total anthocyanin content (TAC)	900W	9min	increased TAC 1.08 times compared to uncooked potatoes	Lachman et al., 2012
	750W	10min	increased TAC 3.06 times compared to uncooked potatoes	Lachman et al., 2013
	700W	8min	decreased 16-19% of TAC compared to uncooked potatoes	Mulinacci et al., 2008
Total starch	700W	8min	19.61-32.14% loss compared to uncooked potatoes	Mulinacci et al., 2008
Resistant starch	700W	8min	2.68-6.31% loss compared to uncooked potatoes	Mulinacci et al., 2008

1.5 Frying and acrylamide formation

Frying has been defined as the immersion of a food product in edible oil above the boiling point of water (Hubbard & Farkas, 1999), with color, texture and flavor development. It is a complex process because of the two mass transfers in opposite directions within the material being fried: for starchy products, water and some soluble material escape from the products and oil enters the food (Blumenthal & Stier, 1991). Acrylamide is a by-product of the Maillard reaction in food processed at temperature >120 °C (Mottram et al., 2002; Stadler et al., 2002) that is a neurotoxin in humans and it has been considered as a probable human carcinogen (Hogervorst et al., 2007; Pedreschi et al., 2004).

The reports of acrylamide intake indicates that fried potato products, bread and bakery products, coffee and breakfast cereals are the food commodities that contribute the most for the dietary acrylamide exposure (Vinci et al., 2012). The content of acrylamide was dependent on factors such as storage, cooking temperature and time, and the amount of reducing sugars and free amino acids like asparagine present in fresh potatoes (Cheong et al., 2005; Halford et al., 2012). Different strategies are proposed for reducing the acrylamide formation in the “Toolbox” by Food Drink Europe (http://www.fooddrinkeurope.eu/uploads/publications_documents/Toolboxfinal260911.pdf). Researches and industry need to find the solutions to reduce or prevent acrylamide formation, but no legal limits have been established for this contaminant in foods, especially the frying potato products.

1.5.1 Pathways for acrylamide formation

Several methanistic pathways have been proposed on the formation of acrylamide during food processing. The major pathway established for acrylamide formation in foods is the Maillard reaction, with the free asparagine and reducing sugar as the main precursors (Mottram et al., 2002; Stadler et al., 2002). The major mechanism of acrylamide formation

involves the reaction of a carbonyl compounds with asparagine, resulting in the decarboxylated Schiff base (Stadler et al., 2004). However, this reaction involves some different highly reaction intermediates resulting in acrylamide formation. Mottram et al. (2002) suggested that α -dicarbonyls are necessary coreactants in the Strecker degradation reaction affording the Strecker aldehyde as the precursor of acrylamide. In addition, Stadler et al. (2002) proposed that glycoconjugates, such as *N*-glycosides and related compounds formed in early phase of the Maillard reaction, as the key intermediates leading to acrylamide. In addition to these pathways, acrylamide can be formed via acrolein and acrylic acid (Yasuhara et al., 2003). It reported that the oxidative lipid degradation released acrolein leading to acrylic acid, which can react with ammonia to give acrylamide. Acrylic acid can also be generated from aspartic acid by the Maillard reaction, in analogy to the formation of acrylamide from asparagine (Stadler et al., 2003).

1.5.2 Factors involved in acrylamide formation

The reducing sugar and asparagines, as the acrylamide precursors, are very important for reducing the acrylamide content in frying potato strips. As one of strategies for reducing the acrylamide formation, the potato cultivars selection is also necessary and very important. The relationship between the asparagine and reducing sugar content in raw potato tubers and acrylamide formation during heat-treatments is complicated. Vinci et al. (2012) reported that asparagine concentrations are relatively in excess compared to reducing sugar content represented the limiting factor in acrylamide formation, and the reducing sugar content will largely determine the acrylamide formation in frying potato products. However, Shepherd et al. (2010) found that asparagine and sugar concentrations contributed approximately equally to the acrylamide formation. Moreover, Halford et al. (2012) suggested that when sugar concentration was relatively high, acrylamide formation during processing was proportional to sugar content, whereas when sugar level was low, acrylamide formation was proportional to the asparagine content. The correlation between reducing sugar and acrylamide formation

has been demonstrated by several researches, but sucrose presented no correlation with the acrylamide level (Vinci et al., 2012; Amrein et al., 2003).

Frying conditions dramatically affect the acrylamide formation of frying potato products. Vinci et al. (2012) reported that the frying time and oil temperature should be controlled in order to reduce the high acrylamide content, and the temperature should not exceed the 170-175 °C, which was due to the lower temperature towards the end of Maillard reaction may reduce acrylamide formation. The longer frying periods would be resulted in higher acrylamide content. Tareke et al. (2002) conducted experiments to monitor the formation of acrylamide during processing, and showed that the acrylamide content was dependent on the temperature and it increased with the temperature increasing. However, some researches found that the higher temperature may decrease the acrylamide formation, and this reduction was not altered in the presence of polymerization inhibitors, indicating that under these conditions the decrease of acrylamide content already occurs below the melting point and is mainly due to degradation rather than polymerization (Becalski et al., 2004; Biedermann et al., 2002).

During frying process, oil is used as the heating medium and an ingredient producing calorific products. Recent studies have indicated that lipid oxidation positively influenced the formation of acrylamide (Zamora & Hidalgo, 2008; Lim et al., 2014). Bouchon et al. (2003) analyzed three different oil fractions to identify the different absorption mechanisms in fried potato cylinders: structure oil which represents the oil absorbed during frying; penetrated surface oil which represents the oil suctioned into the food during cooling after removal from the fryer; surface oil which is the oil that remains on the surface. It concluded that a small amount of oil penetrates during frying because most oil was picked up at the end of the process. The oil uptake was dependent on several factors (frying temperature, moisture content, oil types and particle size). Moyano & Pedreschi (2006) stated that the high temperature causes partial evaporation of water, which moves away from the food and through the surrounding oil, and a certain amount of oil is absorbed by the food. Moreira et

al. (1997) found that higher initial moisture content and smaller particle size produced a final product with higher oil content, and they found the ration of water evaporated and the final oil conten was independent of the oil temperature used. Several procedures have been used to reduce the content of oil in fried potatoes. Rubnov & Saguy (1997) found that adding the fructose reduced the oil uptake after frying. Soaking of potato strips in NaCl solutions and pre-drying of potatoes could also reduce the oil uptake in the final frying products (Moyano et al., 2002).

Color of fried potatoes is an important parameter to be controlled during processing together with textural parameters, oil uptake and acrylamide content. In addition, color of fried potato products is the result of Maillard reaction and it dependent on the reducing sugar content, the frying temperature and period (Marquez & Anon, 1986). Marquez & Anon (1986) found that both reducing sugars and amino acids participated into the color development during frying and the reducing sugars was the limiting factor. Lightness (L^*) of frying potato chips decreased with the frying temperature and time increasing since the chips get darker; a^* increased and means the potato chips get more red, with both the frying temperature and time increasing as a result of Maillard reaction (Pedreschi et al., 2006). They also reported that not only L^* but also a^* presented good correaltions with the acrylamide formation of frying potaton chips ($r^2=0.79$ and 0.83 , respectively). The degree of browning development during frying is related to the pre-treatments employed. Blanching reduces the L^* and a^* values of frying potato products due to the leaching out of reducing sugars previous to frying, inhibiting in this way non-enzymatic browning reactions and leading to lighter and less dark products (Pedreschi et al., 2004).

Pedreschi & Moyano (2005) stated that the normalized maximum force was the parameter used to model the textural changes in the frying potato slices both the initial tissue softening process and the later crust development process. They also found that when frying at $120\text{ }^\circ\text{C}$, potato chips were crispier than potato chips fried at $180\text{ }^\circ\text{C}$, and the blanching significant increased the crispness after frying.

Table 1.5 Effect of frying processing condition on physical and acrylamide formation of potatoes.

Physiochemical composition	Processing conditions			Conclusions	References
	Temperature	Time	oil		
Acrylamide content	170°C	5min	extra virgin olive oil	The acrylamide content ranged from below the limit of detection to 870.33ng/g fw.	Marchettini et al., 2013
	170°C	5min	mixed seed oil	The acrylamide content ranged from 248.36 to 846.79 ng/g fw.	Marchettini et al., 2013
	170°C	5min	peanuts oil	The acrylamide content was from below the limit of detection to 1616.15 ng/g fw.	Marchettini et al., 2013
	150-190°C	6.5-11min	vegetable oil	The reduction of the frying temperature from 190 to 170°C and to 150°C, decreased acrylamide formation with 21% and 66%, respectively.	Pedreschi et al., 2006
	150-190°C	6.5-11min	vegetable oil	Long time blanching treatments such as that of 50°C for 80 min and 70°C for 45min resulted in the lowest levels of acrylamide formation (342 and 538 µg/kg, respectively).	Pedreschi et al., 2006
	150-190°C	6.5-11min	vegetable oil	Strip immersion in sodium pyrophosphate solution of 10 g/L reduced acrylamide formation ranged from 7% to 30%.	Pedreschi et al., 2006
	150-190°C	6.5-11min	vegetable oil	Strip immersion in citric acid solution of 10 g/L reduced significantly acrylamide formation from 28% to 86%.	Pedreschi et al., 2006
	170-190°C	1min25s -1min 50s	sunflower oil	The acrylamide content of potato frying chips increased with the frying temperature (19.6ng/g at 170°C, 39ng/g at 180°C, and 95ng/g at 190°C).	Palazoglu et al., 2010

Table 1.5 Effect of frying processing condition on physical and acrylamide formation of potatoes.

Physiochemical composition	Processing conditions			Conclusions	References
	Temperature	Time	oil		
Color	150-190°C	6.5-11min	vegetable oil	The frying temperature increased from 150 to 190 °C, the potato chips get more red and darker.	Pedreschi et al., 2006
	150-190°C	6.5-11min	vegetable oil	Blanching reduced the L* and a* values of potato chips	Pedreschi et al., 2006
Texture	120-180 °C	-	vegetable oil	Frying at 120 °C, potato chips were crispier than potato chips fried at 180°C.	Pedreschi & Moyano, 2005
Oil uptake	120-180 °C	-	vegetable oil	Potato strips fried at 120°C contained more oil more than chips fried at 180°C.	Pedreschi & Moyano, 2005

1.6 References

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Chapter 2

Objectives

Objectives

The main purpose of this thesis was to study the effect of cooking processes: boiling, baking, microwaving and frying on the physical and chemical properties of potato cultivars consumed worldwide. In order to fulfill the main objective, the following particular objectives were defined,

1. To evaluate eight potato cultivars commonly consumed and study the relationship between their chemical and physical properties to determine their processing aptitude.
2. To study the effect of temperature and time of boiling, baking and microwaving treatments on the nutritional components and physical properties of commercial potato tubers selected.
3. To assess the frying temperature and time on acrylamide content and to study the relationship between acrylamide levels and the factors potentially involved in its formation.

Chapter 3

Working plan

3.1 Working plan

Potatoes are a nutritious foodstuff that is consumed after being cooked. Changes in potato properties related to the cooking methods involved physical and chemical modifications that are not clearly stated in deep. This thesis aimed to evaluate how the common culinary processes affect the properties of several potato cultivars that are widely consumed. Figure 3.1 summarizes the working plan of this research work. At first, it was of interest to assess the differences between eight of the most common consumed potato cultivars to understand their nutritional potential and feasibility to be processed. Secondly, the effects of the conditions of three cooking methods (boiling, baking and microwaving) were evaluated to state how the temperature and time of processing affected the main and minor components of four potato cultivars and their physical properties. Finally, in a third step, frying conditions were evaluated to understand how the properties of four fresh potato cultivars affect the quality of French fries and the acrylamide formation.

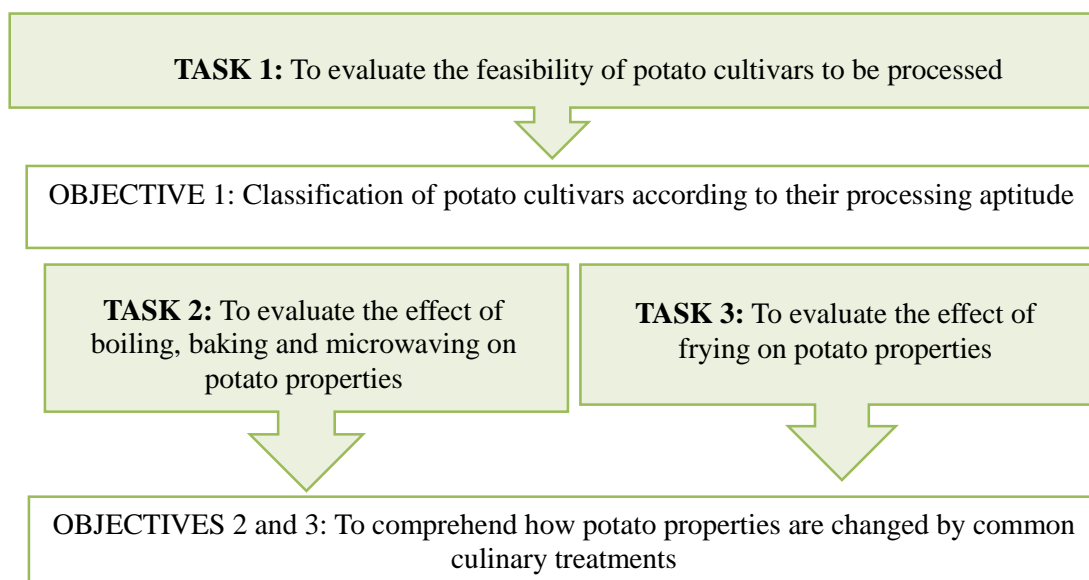


Figure 3.1 Working plan of the research work

3.2 Experiment setup

The experimental setup is showed in Figure 3.2. A set of experiments were conducted to accomplish the goals proposed in the working plan.

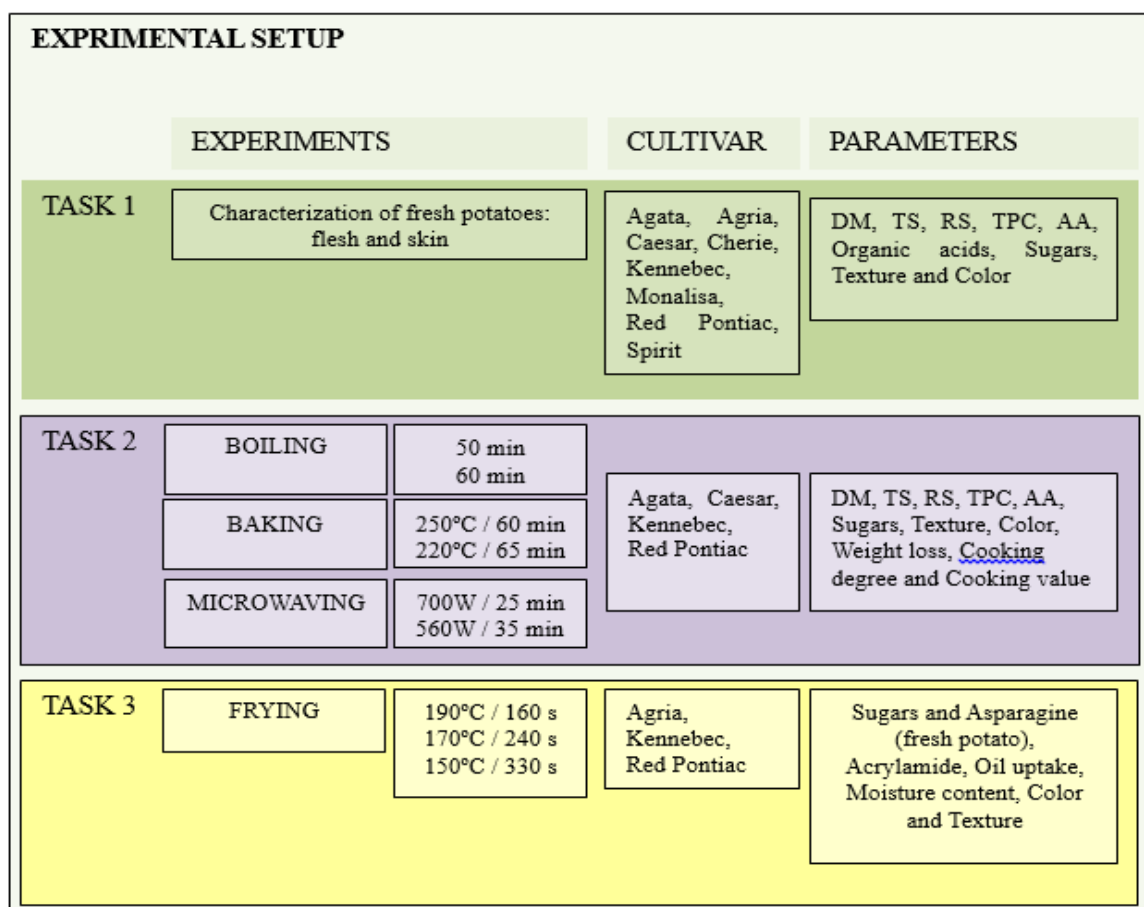


Figure 3.2 Experiment setup

DM=Dry matter; TS= total starch; RS = Resistant starch; TPC = Total phenolics;
AA=Antioxidant activity

Task 1 was an individual experiment. The properties of eight fresh potato cultivars (Red Pontiac, Caesar, Kennebec, Agria, Cherie, Agata, Monalisa and Spirit) commonly consumed were evaluated in order to classify the potato cultivars to establish their processing aptitude.

All the evaluations were conducted in triplicate samples of potatoes. Figure 3.3 shows the potato cultivars used in this study.

In Task 2, four cultivars (Kennebec, Red Pontiac, Caesar and Agata) were selected to evaluate the effect of cooking methods (boiling, baking and microwaving) on the physical and bioactive properties. Experiments were conducted in triplicate for each individual cultivar and analyses were done in triplicate.

In Task 3, Kennebec, Red Pontiac and Agria cultivars were used for the influence of the frying process and potato cultivar on acrylamide formation in French fries. Equally, experiments were conducted in triplicate for each individual potato cultivar and analyses were done in triplicate.

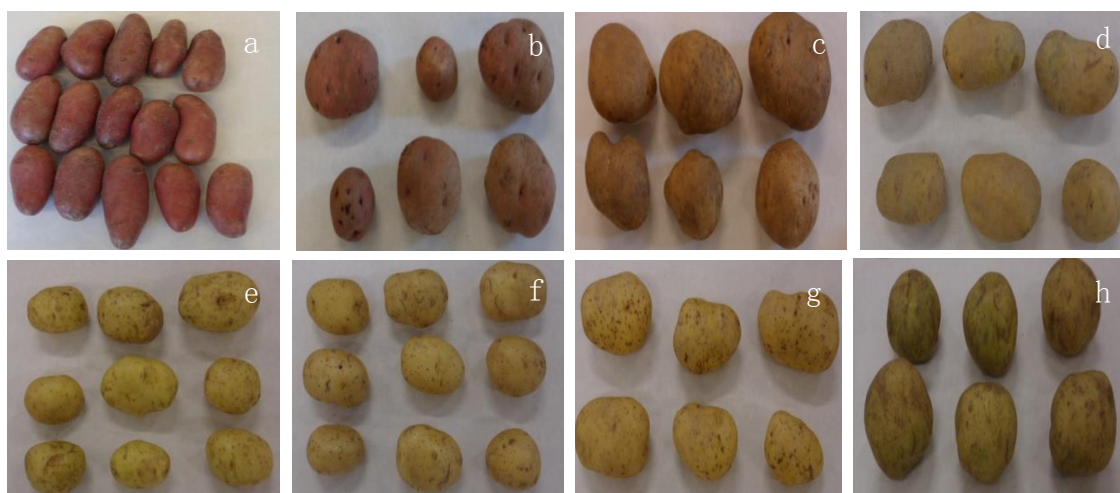


Figure 3.3 Potato cultivars assessed in this study

(a: Cherrie, b: Red Pontiac, c: Agria, d: Caesar, e: Agata, f: Spirit, g: Monalisa, h: Kennebec)

The description of the experimental procedure of each individual task is described in its specific chapter. All the methods of the analyses conducted are also explained in their specific chapter. Equally, the statistical analysis, including Analysis of the variance (ANOVA) and Principal Component Analysis (PCA) are showed in each chapter.

Chapter 4

Classification of potato cultivars to establish their processing aptitude

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Abstract

BACKGROUND: The commercial potato cultivars are diverse not only in their physical characteristics but also in their nutritional compositions and their content of functional compounds (resistant starch, total phenolic content and antioxidant activity), but there is little information about these differences. The aim of this study was to characterise the nutritional value (focusing on carbohydrates and functional compounds) and instrumental parameters of eight potato cultivars consumed in Spain and to determine whether these parameters are useful for classifying the cultivars.

RESULTS: Significant Pearson's correlations were found due to the common and complex interactions between the constituents of potatoes and their properties ($P < 0.05$). Principal component analysis revealed the correlations among the physicochemical properties, and the first two principal components explained 56.84% of the variance among the cultivars studied.

CONCLUSION: The eight cultivars could be classified into three groups: (1) Red Pontiac, Caesar, Kennebec, Agria and Cherie cultivars, (2) Agata and Monalisa cultivars and (3) Spirit cultivar. The results demonstrated that certain nutritional and functional parameters indicated the potential efficacy of different cultivars to satisfy the nutritional needs of consumers, improving the knowledge on the biochemical basis of potato processing to obtain higher-quality products.

Keywords: total starch; resistant starch; total phenolic content; reducing sugars; organic acids

4.1 Introduction

Potatoes (*Solanum tuberosum* L.) are a primary component of the human diet. More than 4000 varieties are cultivated throughout the world. Despite the huge number of potato varieties available, few cultivars have been commercialised. These potato varieties were selected for their feasibility to be marketed and stored. Regular tuber size, high production

ratio, good storage ability, multi-purpose use and consumer acceptance are the main characteristics of the potatoes that producers and sellers have chosen to improve their profits and reduce the waste of potatoes. In addition, the food industry prefers cultivars that can be stored for longer periods. In Spain, the rate of potato consumption is 23.13 kg per person per year and involves mainly stored potatoes with white skin. The predominant variety of potato that is consumed is the Monalisa (26%) cultivar, followed by the Agata (16%) and Kennebec (16%) cultivars and then the Caesar (8%), Agria (4%) and Red Pontiac (3%) cultivars

(http://www.magrama.gob.es/es/alimentacion/servicios/observatorio-de-precios-de-los-alimentos/ESTUDIO_PATATA_14112010_tcm7-182793.pdf).

Freshly harvested potato tubers contain approximately 800 g.kg⁻¹ water and 200 g.kg⁻¹ dry matter. The dry matter of potato tubers is composed of various substances, including starch, sugars, nitrogenous compounds, lipids, organic acids, phenolic compounds, mineral substances and non-starch polysaccharides. The starch content of potatoes varies with the cultivar and its growth stage. As a major constituent of potatoes, starch contributes to the texture, consistency and organoleptic qualities of foods prepared using those (Tharanathan & Tharanathan, 2001). Starch is generally classified as rapidly digestible starch, slowly digestible starch or resistant starch (RS) depending on the rate and extent of its digestion (Song et al., 2010). RS is not digested in the small intestine and therefore reaches the colon, where its fermentation results in the production of short-chain fatty acids, particularly butyric acid. RS was recently recognized as a valuable contributor to dietary fibre intake that is better tolerated than are other soluble fibres. The total sugar content of potatoes is approximately 0.05 g.kg⁻¹ fresh weight, which is in the form of reducing monosaccharides such as D-glucose and D-fructose and non-reducing disaccharides such as sucrose (Lisinska & Leszczynski, 1989). Low storage temperatures may cause an increase in the sugar content of most potato cultivars. The organic acids in potato tubers are carbonaceous compounds with high metabolic activity, and some of them are related to each other. The main organic acids in potato tubers are citric, malic, tartaric, oxalic, fumaric and succinic acids. The

content of citric acid in potato tubers is higher than that of the other acids, and it plays an important role as an antioxidant by inhibiting the oxidative enzymatic browning process (Wichrowska et al., 2009).

Phenolic compounds are members of a large group of minor plant products that play an important role in determining organoleptic properties. In potato tubers the phenolic compounds are located mainly in the skin and adhesive tissue cortex, and the concentrations of phenolic components decrease toward the centre of the tuber (Friedman, 1997). However, potato skins are often wasted as a by-product of the potato-processing industry (i.e. frying of potato chips) or by consumers. Lopez-Cobo et al. (2014) studied the phenolic compounds of potato skin and stated that the potato skin merited more attention. Physicochemical properties contained in potato tubers that may act as antioxidants in the human diet have been intensively studied (Lachman & Hamouz, 2000; Brown, 2005). High positive correlations between the level of antioxidant activity (AA) and the total phenolic content (TPC) were found by Reyes et al. (2005) who stated that phenolic compounds were mainly responsible for the antioxidant activity of potatoes. The antioxidant activities of potatoes vary among potato genotypes with different flesh colours, and purple potatoes tend to be associated with a high level of total AA (Teow et al., 2007).

In summary, potatoes are a healthy component of a varied diet because they are a relatively low-calorie food containing a variety of dietary fibre nutrients and antioxidants. However, there is sparse information about the correlations among the textural parameters, carbohydrate components, phenolics and antioxidant capacity of commonly consumed potato cultivars. The main purposes of this study were (1) to evaluate the instrumental parameters, carbohydrates and functional content of eight commercial cultivars consumed in Spain, focusing on the starch profile (RS, total starch (TS)), functional content (TPC, AA), colour and texture, and (2) to establish possible correlations between nutrients as a distinguishing feature of different potato varieties for determining their aptitude for processing.

4.2 Materials and methods

4.2.1 Chemicals

All chemicals and solvents used were of analytical grade. Oxalic acid, fumaric acid, tartaric acid, malic acid, citric acid, lactic acid, D-(+)-fructose, D-(+)-glucose, sucrose, gallic acid 1-hydrate, Folin-Ciocalteu reagent, sodium dihydrogen phosphate, anhydrous sodium carbonate, high-performance liquid chromatography (HPLC)-grade acetonitrile and 370 mL.L⁻¹ chloridric acid were purchased from Panreac Applichem (IWT Group, Barcelona, Spain). Methanol and anhydrous disodium hydrogen phosphate were supplied by Scharlau Chemie (Scharlab SL, Barcelona, Spain). Thermostable amyloglucosidase (GOPOD) reagent buffer, GOPOD reagent enzymes, D-(+)-glucose standard solution, amyloglucosidase and pancreatic α -amylase were purchased from Megazyme International (Bray, Ireland). Fluorescein, 2,2-azobis (2-amidinopropane) dihydrochloride (AAPH) and 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox) were obtained from Acros Organics (Thermo Fisher Scientific Inc., Waltham, MA, USA).

4.2.2 Sample preparation

Potato samples

Potato tubers (*S. tuberosum* L.) of eight cultivars that are commercialized in Spain (Agata, Agria, Caesar, Cherie, Kennebec, Monalisa, Red Pontiac and Spirit) were obtained from Mercabarna (Mercados de Abastecimientos de Barcelona SA, Barcelona, Spain). All potatoes were grown in Europe and had the same postharvest storage conditions. Randomly chosen samples of 10 kg of each potato cultivar were provided. Table 4.1 shows the physical characteristics of the potato cultivars. The average weight of the tubers ranged from 134 to 337 g, except for that of the Cherie cultivar, which was less than 100 g. The colour of the skin of the tubers was white to yellow, except for that of the Red Pontiac and Cherie cultivars, which was red. The flesh colour ranged from white to yellow. Two of the cultivars (Agria and Caesar) were defined as mealy, which might be due to their high starch content,

while the others (Agata, Cherie, Kennebec, Monalisa, Red Pontiac and Spirit) were defined as multi-purpose (useful for boiled and baked products).

Each selected potato tuber was washed, the potatoes were hand peeled and the potato flesh was cut into small strips (1 cm × 1 cm × 5 cm). The potato flesh strips and the skin peels were lyophilised using a freeze-drying instrument (Cryodos 45, Telstar, Terrassa, Spain) and packed in plastic bags. The lyophilized powders were maintained at -20 °C until further use.

Table 4.1 Description of the potato samples

Cultivar	Cultivar Origen ^a	Shape ^a	Weight (g) ^b	Color ^a Flesh and Skin	Cooking type ^a
Agata	Netherlands	oval to round	175.09±8.21	light yellow /white to yellow	multi-purpose
Agria	Germany	oval to long	218.70±7.75	Yellow /white to yellow	mealy (floury)
Caesar	Netherlands	oval to round	337.60±9.25	light yellow /white to yellow	mealy (floury)
Cherie	France	very long	79.47±4.75	yellow/red	multi-purpose
Kennebec	United States	oval to round	200.20±6.78	White /white to yellow	mealy to multi-purpose
Monalisa	Netherlands	oval to long	229.80±5.43	light yellow /white to yellow	multi-purpose
Red Pontiac	United States	round	226.50±7.89	light yellow /red	multi-purpose
Spirit	France	oval to round	134.70±5.67	light yellow /white to yellow	-

^a Source: European Cultivated Potato database (2014)

^b Values are expressed as the mean value± standard deviation of 10 individual potatoes

Extraction of phenolic compounds, sugars and organic acids

Methanolic extracts were obtained using the procedure described by Andre et al. (2009) with slight modifications. In brief, the lyophilized powder of each sample was mixed and chilled, and 1 g was removed for extraction. Solid-liquid extraction was performed using 10 mL of acidified methanol/water (80:20 v/v) containing 0.1 g.L⁻¹ HCl by sonication (Bandelin Sonopuls GM70, Berlin, Germany) for 14 min in an ice bath. After sonication, the

extracts were centrifuged (Selecta, Barcelona, Spain) at $2313 \times g$ for 10 min at 4 °C. The supernatant was filtered through Whatman No. 1 filter paper and the pellet was re-extracted as before. The two liquid extracts were mixed and evaporated to dryness using a rotary evaporator at 40 °C (Laborota 4000 Efficient, Schwabach, Germany). The organic residue was brought to 5 mL with acidified water containing 0.1 g.L⁻¹ HCl and stored at -20 °C until further analysis. All samples were extracted in triplicate. The potato skin and flesh extracts were used for analysis of the phenolic compound content and antioxidant capacity. The flesh extracts were also used for the measurement of sugar and organic acid contents.

4.2.3 Instrumental analysis

Colour evaluation

The colour of potato samples was measured using a Minolta CR-400 colorimeter (Osaka, Japan) in CIE Lab space. The L* (lightness), a* (greenness (-) to redness (+)) and b* (blueness (-) to yellowness (+)) values were evaluated at three different positions. Values for the parameters hue angle (H°) and chroma (C) were calculated as follows: $H^\circ = \tan^{-1}(b^*/a^*)$ and $C = (a^{*2} + b^{*2})^{1/2}$. Six measurements were taken for each potato sample, and results were expressed as mean \pm standard deviation (SD).

Texture analysis: texture profile analysis and shear force

Texture profile analysis (TPA) of fresh samples was performed using a 75 mm diameter cylindrical plunger probe. Six potato cylinders (length 10 mm, diameter 10 mm) were analysed for each potato sample. The test conditions were a speed of 0.83 mm.s⁻¹, a rest period of 5 s between cycles and a trigger force of 5 g. The maximum extent of deformation was 40% of the original length (Alvarez & Canet, 2000). Four TPA parameters were determined from each curve as described by Bourne (1978): hardness (peak force of the first compression cycle), cohesiveness (ratio of positive force area during the second compression to that during the first compression), springiness (ratio of time duration of

force input during the second compression to that during the first compression) and chewiness (hardness multiplied by cohesiveness multiplied by springiness). Six potato cylinders were analysed for each potato sample, and results were expressed as mean \pm SD.

The flesh shear force of potato cultivars was measured using a texture analyser (TA.XT Plus, Stable Microsystems, Godalming, UK) equipped with a Warner-Bratzler probe as described previously (Singh & Kaur, 2009). The test conditions were a speed of 1 mm.s⁻¹, a target distance of 22 mm into the sample and a trigger force of 2 g. The potato strips were cut vertically by the probe, and the shear force was set as the maximum force (N). Six potato strips were tested for each potato sample, and results were expressed as mean \pm SD.

4.2.4 Potato component analysis

Drymatter and pH

Drymatter (DM) content was determined by a gravimetric method (AOAC method 931.04) and expressed as g.kg⁻¹. pH was determined according to AOAC method 981.12. All analyses were conducted in triplicate, and results were expressed as mean \pm SD.

Determination of total starch and resistant starch contents

TS and RS contents were analysed through their enzymatic hydrolysis to D-glucose using AOAC methods 996.11 (amyloglucosidase/ α -amylase method) and 2002.02 respectively. D-(+)-Glucose was oxidised to D-gluconate, which was quantitatively measured from the absorbance at 510 nm of a colorimetric reactant. Results of the TS and RS analyses were expressed as g.kg⁻¹ lyophilised weight (LW). Each sample was analysed in triplicate.

Sugar analysis

The sugar content of potato samples was analysed using a Hewlett Packard Series 1100 HPLC instrument (Santa Clara, CA, USA) equipped with a Beckman 110B injector and a Beckman refraction index detector (Brea, CA, USA). Separation was performed on a

Phenomenex Luna (Torrance, CA, USA) column (250 mm× 4.6 mm i.d.) following the method of Rodriguez-Galdon et al (Rodriguez-Galdon et al., 2010). Briefly, the liquid extracts were filtered through a 0.45 µm membrane filter, and 20 µL of each filtrate was injected. The mobile phase consisted of acetonitrile/water (78:22 v/v) at a flow rate of 1.2 mL.min⁻¹. Individual sugars were identified by comparing their retention times with those of external standards, and quantification was conducted through calibration using the external standards. Each extract was analysed in triplicate. Sugar contents were expressed as g.kg⁻¹ LW.

Organic acid analysis

Organic acid contents were determined using the same protocol as for sugar contents, except that detection was conducted using a Beckman 166 UV–visible detector set to 210 nm as described by Rodriguez-Galdon et al. (2010). Organic acid contents were expressed as g.kg⁻¹ LW.

Total phenolic content analysis

The TPC of potato skin and flesh extracts was determined using a modified version of the Folin-Ciocalteu assay (Singleton et al., 1999). Gallic acid was used as the standard and was diluted with distilled water to obtain the range of concentrations appropriate for a standard curve. A 20 µL aliquot of sample extract, gallic acid calibration standard or blank material was placed in a plastic cuvette with 1.58 mL of distilled water and 100 µL of Folin–Ciocalteu reagent. After 5 min of incubation, 300 µL of 200 g.L⁻¹ sodium carbonate was added and the solution was incubated for 2 h at room temperature. Then the absorbance at 765 nm was measured using a Nicolet Evolution 300 spectrophotometer (Thermo Electron Corporation, Basingstoke, UK). Results were expressed as g gallic acid equivalent (GAE).kg⁻¹ LW.

Analysis of antioxidant activity of potato skin and flesh extracts

The AA of extracts was evaluated using the oxygen radical absorbance capacity assay as described by Gorjanovic et al. (2013). Briefly, 13.5 μL of each diluted sample or standard solution (Trolox at five different concentrations ranging from 6.25 to 500 $\mu\text{mol.L}^{-1}$) was mixed with 135 μL of 9.57×10^{-2} $\mu\text{mol.L}^{-1}$ fluorescein in a well of a 96-cell plate; the plate was incubated at 37 °C for 10 min, then 50 μL of 153 mmol.L^{-1} AAPH was added to each well to initiate the reaction. The fluorescence was measured every 2 min for 120 min at 37 °C, with emission and excitation wavelengths of 485 and 530 nm respectively, using a microplate fluorescence reader (Synergy™ Multi-detection Microplate Reader, BioTek Instruments, Winooski, VT, USA) until the decay of the kinetic curve was complete. The area under the curve (AUC) and the net AUC ($\text{AUC}_{\text{standard}} - \text{AUC}_{\text{blank}}$) were calculated for each standard or sample. A blank measurement was taken and a linear standard curve (five standards) was created for every run. Results were expressed as g Trolox equivalent (TE). kg^{-1} LW. The reagents, standards and diluted samples were prepared using phosphate buffer (pH 7.4). Each extract was analysed in triplicate.

4.2.5 Statistical analysis

The data reported are the mean values of the results of triplicate analyses. The coefficient of variation of the chemical data was less than 5%. Variations among the contents of the potato components were evaluated using one-way analysis of variance (ANOVA). Differences between mean values were evaluated using Tukey's honestly significant difference (HSD) test with 95% confidence level. Pearson's correlation analysis was conducted to study the relationships among variables. Both analyses were conducted using Minitab 16 statistical software (Minitab Inc., State College, PA, USA). Principal component analysis (PCA) was conducted to determine the relationships among variables, which were analysed using STAT-ITCF statistical software (ITCF, Bordeaux, France).

4.3 Results and discussion

4.3.1 Instrumental parameters

Colour characteristics

Colour is an important quality parameter for raw potato tubers that is affected by certain pre- and postharvest factors and by the type of cultivar. The chroma and hue angle values of the tubers of the different potato cultivars varied considerably (Table 4.2). The chroma values of the yellow and light yellow tubers were higher than those of the white tubers, with the exception of the Spirit tuber. The tuber chroma values increased from the Red Pontiac cultivar to the Agria cultivar (from 13.47 to 30.29, respectively). Our results were similar to those of Cabezas-Serrano et al. (2009) who found that the chroma values of the tubers of five industrial potato cultivars ranged from 17.1 to 31.0. Among the cultivars analysed, the highest hue angle value was obtained for Agata tubers (light yellow), followed by Monalisa (light yellow) and Spirit (white) tubers, and the lowest value was obtained for Cherie (yellow) tubers. The hue angle values of the tubers of the other cultivars were not significantly different ($P>0.05$).

Texture: TPA and shear force

The values obtained from the TPA of the raw potatoes varied considerably among the eight cultivars (Table 4.2). Their hardness ranged from 123.89 to 156.80 N, and these results were consistent with those of Bordoloi et al. (2012). Spirit showed greater hardness and shear force, while Agata showed the lowest hardness and shear force of the tested cultivars. Therefore significant correlation was found between shear force and hardness ($r=0.838$, $P<0.05$). In addition, the Spirit cultivar also had the highest cohesiveness, springiness and chewiness values among all cultivars. The values of cohesiveness and springiness of all cultivars tested were smaller than other parameters, but these values were significantly different ($P<0.05$). Shear force also significantly correlated with chewiness ($r=0.708$, $P<0.05$). The differences in this textural property among the potato cultivars may be due to

their differing DM content (Casanas et al., 2002). Texture is a very important parameter in the cooking quality of potatoes. Mealiness was used to describe the texture of boiled, baked and oven-fried potatoes, while hardness was also judged regarding quality (Kreutzmann et al., 2011). According to Kaur et al. (2002), potato cultivars with greater mealiness showed higher hardness and cohesiveness. The textural changes that occur during cooking are associated with the gelatinization and retrogradation behaviour of starch and with enzymatic and non-enzymatic changes in pectin (Kreutzmann et al., 2011).

Table 4.2 Color and texture profile analysis parameters of raw potatoes from different cultivars.

Cultivar	Chroma	Hue angle (°)	Shear force (N)	Hardness (N)	Cohesiveness	Springiness (mm)	Chewiness (N.mm)
Agata	22.08±2.49c	102.19±0.35a	38.15± 4.86d	123.89±16.61b	0.44±0.25ab	0.64±0.05ab	34.56±7.79ab
Agria	30.29±3.13a	98.567±0.57e	50.12±3.51bc	156.80±17.80a	0.46±0.03ab	0.54±0.02d	36.40±10.48ab
Caesar	17.47±1.75d	99.560±1.28cd	55.64±6.77ab	152.96±16.36a	0.43±0.05ab	0.60±0.04bc	39.33±5.07ab
Cherie	25.73±3.55b	97.25±1.60f	53.55±5.92abc	155.57±17.45a	0.45±0.02ab	0.61±0.02ab	43.03±6.03ab
Kennebec	14.29±1.29e	99.66±0.78bcd	49.65±5.72bc	140.04±12.98ab	0.42±0.17ab	0.60±0.05b	45.00±3.55ab
Monalisa	25.93±3.15b	100.51±1.6b	47.06±4.63c	139.28±20.68ab	0.45±0.03ab	0.63±0.02ab	39.22±7.28ab
Red Pontiac	13.47±1.63e	98.89±1.28de	46.76±4.35c	151.13±19.73a	0.38±0.09b	0.55±0.03cd	31.50±8.72b
Spirit	27.92±2.30b	100.24±1.05bc	58.59±7.35a	156.30±35.83a	0.49±0.02a	0.66±0.02a	52.43±10.09a

Values are expressed as the mean value ± standard deviation. Results with the same superscripts in a column did not differ significantly ($p < 0.05$).

4.3.2 Dry matter and carbohydrate contents of commercial potatoes

The DM content of the potatoes ranged from 230 g.kg⁻¹ for the Spirit cultivar to 184 g.kg⁻¹ for the Agata cultivar. All cultivars except the Agata variety contained more than 200 g.kg⁻¹ DM, and significant differences in the DM contents of the cultivars were found, as shown in Table 4.3 ($P < 0.05$). Usually, commercial varieties of potatoes are selected according to their DM content, but this parameter can be affected by the storage and growing areas. Stored

Agata and Agria tubers from Italy had similar contents of DM (Cabezas-Serrano et al., 2009), but Agria tubers purchased in New Zealand had a higher content of DM (Bordoloi et al., 2012).

Starch is the main component of DM, with a concentration of approximately 600 g.kg⁻¹ (Liu et al., 2007). The content of TS, which is also the major carbohydrate component of potatoes, ranged from 681 (Agata) to 752 (Spirit) g.kg⁻¹ LW, as shown in Table 4.3. The cultivated potatoes had a mean content of 188 g.kg⁻¹ starch on a fresh weight (FW) basis, with a range from 100 to 300 g.kg⁻¹ (Camire et al., 2009). Among the studied potatoes with starch contents lower than the mean value, the tubers of the Spirit and Agata cultivars contained 173 and 125 g.kg⁻¹ starch FW respectively. The TS contents observed in this study were similar to those reported by Bordoloi et al. (2012) for four commercial varieties.

The RS in raw potatoes is defined as type 2 (RS2), which comprises ungelatinised resistant granules that are slowly hydrolysed by α -amylase (Fuentes-Zaragoza et al., 2010). In this study the RS content of the potatoes ranged from 482 (Agria) to 610 (Cherie) g.kg⁻¹ LW (Table 4.3). Previous reports noted that fresh potatoes contain 691-764 g.kg⁻¹ RS (Lante & Zocca, 2010; Garcia-Alonso & Goni, 2000), but there are sparse data about the differences among potato cultivars. Our results showed that the potatoes of the cultivars studied contained less RS than was previously reported and there were significant differences between the RS contents of the cultivars ($P < 0.05$). Notably, the fraction of RS comprised 65–85% of the TS in the potatoes of the eight cultivars assessed.

Significant differences were found in the sugar content of the potatoes of the eight cultivars tested ($P < 0.05$). The concentration of glucose (1.20-23.50 g.kg⁻¹ LW) was slightly higher than that of fructose in all cultivar samples. Their fructose content ranged from 0.80 to 14.1 g.kg⁻¹ LW and their sucrose content ranged from 1.40 to 4.5 g.kg⁻¹ LW. Plata-Guerrero et al. (2009) analysed the glucose, fructose and sucrose content of the potatoes of four commercial cultivars and also found that the content of glucose (0.28-1.20 g.kg⁻¹ FW) was higher than that of fructose (0.27-0.90 g.kg⁻¹ FW) and sucrose (0.26-0.40 g.kg⁻¹ FW). These results may be due to the high concentration of fructokinase in potatoes; this enzyme could

redirect fructose into the hexose phosphate pathway (Kumar et al., 2004). Our data showed that the reducing sugar (glucose and fructose) content of the tubers ranged from 2.02 to 37.6 g.kg⁻¹ LW and the reducing sugar contents of the Agata and Monalisa tubers were significantly higher than those of the other cultivars. Wegener et al. (2009) analysed a variety of coloured potato cultivars and found that the content of reducing sugars in their tubers ranged from 0.26 to 0.75 g.kg⁻¹ FW. Whereas the cultivar type and storage conditions had a notable effect on the equilibrium between free sugars and starch in tubers, Kumar et al. (2004) did not observe changes in the concentration of reducing sugars in tubers during the first 3 days of storage at low temperatures (4-6 °C). Endo et al. (2006) observed that, during storage at temperatures lower than 8 °C, the content of reducing sugars increased markedly in all cultivars studied. Furthermore, reducing sugars affect potato processing, such that the higher the reducing sugar content, the higher the level of browning after frying. Additionally, Muttucumaru et al. (2014) proposed that, in potatoes, sugars are more important than free asparagine as acrylamide precursors, because other amino acids present in potatoes may play a role in the formation of this contaminant. Therefore the tubers of commercialised cultivars that develop a high content of reducing sugars during storage may be a potential risk for acrylamide formation during cooking (i.e. baking or frying).

Table 4.3 Dry matter content, total starch content, resistant starch content and sugar composition of the potato cultivars

Cultivar	DM (g·kg ⁻¹)	TS (g·kg ⁻¹ LW)	RS (g·kg ⁻¹ LW)	Sugars (g·kg ⁻¹ LW)			Reducing sugars (g·kg ⁻¹ LW)
				Fructose	Glucose	Sucrose	
Agata	183.61±12.11c	681.30±12.61b	544.63±7.91d	14.10±0.51a	23.50±0.90a	4.00±0.60a	37.60±1.41a
Agria	209.53±2.30b	715.66±10.30ab	482.31±14.22c	0.80±0.11f	1.20±0.10f	2.83±0.21bc	2.02±0.21e
Caesar	215.32±3.20b	718.18±7.92ab	599.73±30.50a	2.91±0.10de	3.96±0.10de	2.52±0.20c	6.87±0.20cd
Cherie	222.08±0.73ab	751.11±11.23a	607.45±12.73a	3.56±0.10cd	6.35±0.20c	3.25±0.10b	9.91±0.20c
Kennebec	215.70±3.71ab	731.92±20.30a	574.50±18.17ab	2.53±0.20e	4.60±0.30d	1.46±0.20d	7.13±0.50cd
Monalisa	209.96±1.15b	731.57±18.45a	560.95±23.72ab	12.33±0.30b	1.84±0.30b	4.00±0.10a	14.17±0.60b
Red Pontiac	214.09±3.92b	737.71±10.48a	567.85±12.56ab	3.75±0.10c	4.83±0.10d	4.51±0.10a	8.58±0.20c
Spirit	229.77±2.64a	751.96±16.81a	585.23±14.22ab	2.74±0.10e	2.84±0.10e	1.64±0.20d	5.58±0.20de

Values are expressed as the mean value ± standard deviation (n=3)

Results in the same row with the same superscript (a-f) were not statistically significant ($p < 0.05$)

DM= dry matter; TS=total starch; RS = resistant starch

4.3.3 Correlations among carbohydrate content, dry matter content and texture of commercial potatoes

Pearson's correlations were calculated to evaluate the relationships among the components of the potatoes. The TS content of the potatoes was highly positively correlated with their DM content ($r=0.722$, $P<0.01$), in agreement with the results of Bordoloi et al. (2012). However, a less significant correlation was found between the DM and RS contents of the potatoes ($r=0.441$, $P=0.031$), which may be due to the content of RS being dependent on the physicochemical properties of the starch (Noda et al., 2008). Finally, the level of correlation between the contents of RS and TS in the potatoes ($r=0.417$, $P<0.01$) was similar to that found for the RS and DM contents.

As expected, the glucose content was significantly positively correlated with the fructose content ($r = 0.993$, $P<0.01$). There were negative correlations between the reducing sugar content and the contents of TS ($r=-0.515$, $P<0.01$) and DM ($r=-0.727$, $P<0.05$).

The potatoes that had higher starch and DM contents (such as Spirit potatoes) were observed to be much harder and more cohesive than those with low levels of these components. Significantly positive Pearson's correlations were found between the hardness and shear force levels and the DM content of raw potato tubers ($r = 0.824$, $P < 0.05$ and $r = 0.915$, $P < 0.01$ respectively), while the correlations between the hardness and shear force levels and the TS content were also high ($r = 0.700$ and 0.734 respectively, $P < 0.05$).

4.3.4 Organic acids and pH

As Table 4.4 shows, the pH values of the tubers ranged from 5.89 to 6.30. The correlation between the organic acid contents and the pH level was significant ($r = 0.555$, $P = 0.03$). The organic acids are biologically important because they participate in various metabolic processes, such as the Krebs cycle. These compounds affect the acidity and pH of potatoes, depending on their concentration and their pK_a (Rodriguez-Galdon et al., 2010).

The concentrations of the six most abundant organic acids (oxalic, tartaric, malic, lactic, citric and fumaric acids) in the potato tubers are listed in Table 4.4. Citric acid was the most abundant organic acid in all tested potato cultivars. The ranges of oxalic, tartaric, malic and lactic acid contents were similar; however, significant differences in the organic acid contents of the cultivars were found ($P < 0.05$). Fumaric acid was the least abundant organic acid, and there were no significant differences in its content among the cultivars ($P > 0.05$). Rovers and Guttman (1992) reported citric acid contents ranging from 6.0 to 20 g.kg^{-1} dry weight (DW), which is consistent with our finding of a range of 7.1-11.3 g.kg^{-1} LW; their malic acid content ranged from 1.0 to 6.0 g.kg^{-1} DW, which was slightly higher than our results (with a range of 0.7-1.3 g.kg^{-1} LW). The tartaric and oxalic acid contents found in our study are similar to those of Wichrowska et al. (2009) and Rodriguez-Galdon et al. (2010) respectively. None of the previous studies reported the presence of lactic acid.

The concentrations of individual organic acids differed among the potato cultivars. In general, Agata potatoes presented a higher content of citric and lactic acids, and Agria

potatoes had a higher content of tartaric and oxalic acids. A higher content of malic and fumaric acids was found in Caesar potatoes. Organic acids (lactic, citric, oxalic, tartaric and fumaric acids) have been described as strong antimicrobial agents against psychrophilic and mesophilic microorganisms in fresh-cut fruit and vegetables (including potatoes) (Bari et al., 2005). The decreasing of citric acid in potato tubers, as well as, the tendency of boiled potatoes to darken, was attributed to the non-enzymatic process of antioxidants (Lisinska & Aniolowski, 1990).

Pearson's correlation analysis showed positive and significant correlations between the oxalic and tartaric acid contents ($r=0.768$, $P<0.05$), the citric and oxalic acid contents ($r=0.661$, $P<0.05$) and the AA level and total organic acid content ($r=0.565$, $P<0.05$), but no significant correlations ($P>0.05$) were found between the total organic acid content and the values of the other parameters studied.

Table 4.4 Organic acids and pH of the potato cultivars

Cultivar	Organic acids (g·kg ⁻¹ LW)						Total acids (g·kg ⁻¹ LW)	pH
	Oxalic acid	Tartaric acid	Malic acid	Lactic acid	Citric acid	Fumaric acid		
Agata	1.60±0.10b	1.61±0.80bc	1.20±0.10ab	1.22±0.50a	11.30±2.40a	0.40±0.10a	17.33±4.00a	6.11±0.02c
Agria	1.92±0.10a	4.64±0.20a	0.70±0.10d	0.80±0.10ab	9.91±0.30ab	0.31±0.00a	18.28±0.80a	6.30±0.01a
Caesar	1.51±0.10b	1.53±0.10bc	1.32±0.10a	0.51±0.10bc	7.22±0.40b	0.40±0.30a	12.49±1.10bc	6.09±0.02c
Cherie	1.72±0.10b	2.33±0.10b	0.83±0.10cd	0.82±0.00ab	7.10±0.30b	0.30±0.00a	13.10±0.60bc	6.02±0.02d
Kennebec	0.93±0.10c	1.14±0.00c	1.00±0.00bc	0.10±0.00c	7.34±0.10b	0.21±0.00a	10.72±0.20c	6.02±0.02d
Monalisa	1.02±0.10c	1.00±0.10c	0.80±0.10cd	0.80±0.00ab	11.25±0.10a	0.32±0.00a	15.19±0.40ab	5.89±0.01f
Red Pontiac	1.54±0.10b	1.82±0.00bc	0.72±0.10d	0.73±0.00abc	8.43±0.10ab	0.20±0.00a	13.44±0.30bc	5.97±0.03e
Spirit	1.66±0.10b	2.00±0.70bc	1.00±0.10bc	0.80±0.40abc	9.65±2.70ab	0.42±0.10a	15.53±4.10ab	6.20±0.01b
<i>Average</i>	<i>1.49</i>	<i>2.01</i>	<i>0.95</i>	<i>0.72</i>	<i>9.02</i>	<i>0.32</i>	<i>14.51</i>	—

Values are expressed as the mean value ± standard deviation (n=3)

Results in the same row with the same superscript (a-f) were not statistically significant (p <0.05) according to the classification

4.3.5 Total phenolic content

The phenolic content of potatoes depends primarily on the genotype and the growing location, but certain methods of extraction and sample preparation, such as vigorous extraction methods, can lead to an apparent increase in the phenolic content (Rumbaoa et al., 2009). According to Ji et al. (2012), with the exception of a few cultivars, the selected potatoes had higher concentrations of phenolics in the skin than in the flesh, often twice as much. Potato skins are a rich source of phenolic compounds, but much of the phenolic content of potatoes is wasted in the manufacture of some potato products, such as potato

chips. The effect of cultivar on TPC and the differences in TPC between the skin and flesh are shown in Table 4.5.

The TPC of potato skins ranged from 3.8 to 6.7 g GAE.kg⁻¹ LW. These results were in accordance with those of Wu et al. (2012), who reported that the TPC of potato skins ranged from 0.76 to 7.88 g GAE.kg⁻¹ DW. In general, significant differences in TPC between the cultivars were found ($P<0.05$). Apart from the Caesar and Agata cultivars, the white- to yellow-skinned cultivars had a lower TPC than the red-skinned cultivars, as expected. Several studies have reported that red- or purple-skinned potatoes contain higher amounts of phenolic compounds (anthocyanins) compared with yellow-skinned cultivars (Perla et al., 2012). The high phenolic content of some white- to yellow-skinned cultivars (Caesar and Agata) may be explained by the differences in their phenolic compound profiles.

As shown in Table 4.5, the TPC of potato flesh ranged from 0.89 ± 0.02 (Kennebec) to 1.73 ± 0.04 (Agata) g GAE.kg⁻¹ LW, which was lower than the range reported by Ji et al. (2012) (1.60-8.40 g GAE.kg⁻¹ DW). Ah-Hen et al. (2012) analysed Shepody and Desiree cultivars and found that the TPC of peeled potatoes varied from 1.91 to 18.6 g GAE.kg⁻¹ DW, which was also higher than the range we observed. The TPC of different potato cultivars clearly varied widely. According to Teow et al. (2007), purple-fleshed sweet potato clones had the highest TPC, followed in order by orange-, yellow- and white-fleshed clones. Negative correlations were found between the DM and TS contents and the TPC content ($r=-0.585$, $P<0.05$ and $r=-0.456$, $P<0.05$ respectively).

Table 4.5 Total phenolic content (TPC) and antioxidant activity (AA) in flesh and skin of potato cultivars

Potato cultivars	TPC content (g GAE.kg ⁻¹ LW)		Antioxidant activity (ORAC) (g TE.kg ⁻¹ LW)	
	Skin	Flesh	Skin	Flesh
Agata	6.13±0.05bc	1.73±0.04a	70.08±13.06ab	10.79±1.42a
Agria	4.41±0.15f	0.99±0.06ef	40.57±16.52bc	9.59±1.02ab
Caesar	6.69±0.07a	1.13±0.05c	74.61±15.09ab	8.66±0.62abc
Cherie	5.99±0.12c	1.35±0.03b	61.82±11.89abc	7.93±0.25bc
Kennebec	4.94±0.14e	0.89±0.02f	47.45±10.46abc	4.83±1.32d
Monalisa	3.80±0.08g	1.02±0.04de	26.03±2.62c	7.78±0.27bc
Red Pontiac	6.34±0.08b	1.42±0.02b	77.04±20.09 ^a	9.91±0.82ab
Spirit	5.56±0.06d	1.11±0.05cd	58.62±9.81abc	6.36±1.05cd

Values are expressed as the mean values ± standard deviation (n=3)

Values with the same superscripts in a column did not differ significantly ($P<0.05$).

GAE = gallic acid equivalents; TE = trolox equivalents.

4.3.6 Antioxidant activity

There are some difficulties in measuring the true antioxidant status of food products *in vivo*. The AA of foods or food components have been evaluated using *in vitro* chemical models. There are two major mechanisms to explain how antioxidants deactivate free radicals, namely hydrogen atom transfer and single-electron transfer (Ah-Hen et al., 2012). Two assays of the AA are generally used: the ORAC (oxygen radical absorption capacity) assay to determine the hydrogen atom transfer activity and the FRAP (ferric-reducing antioxidant power) assay to determine the single-electron transfer activity. However, the ORAC assay is considered more closely related to a human biological assay (Prior et al., 2005).

The AA of potato skin and flesh extracts are presented in Table 4.5. The AA in the flesh and skin extracts of the potato cultivars ranged from 4.83 to 10.79 g TE.kg⁻¹ LW and from 26.03 to 77.04 g TE.kg⁻¹ LW respectively, and significant differences between the values for different cultivars were found ($P<0.05$). The flesh extracts of the yellow and light yellow

cultivars exhibited significantly higher AA than those of the white-fleshed potato cultivars. The highest AA was found in the Agata flesh sample (10.79 g TE.kg⁻¹ LW). Apart from the potato, other foods such as sorghum and sweet potato also show a similar relationship between the colour intensity and the AA (Teow et al., 2007).

Pearson's correlations between the TPC and ORAC values of the skin and flesh samples were evaluated. The results showed positive correlations between the ORAC values of the potato skins and their TPC ($r=0.984$, $P<0.01$) and between the ORAC values of the potato flesh samples and their TPC ($r=0.659$, $P <0.01$). High correlations between the TPC and AA have been reported for various food commodities such as sorghum ($r=0.971$), cactus pear ($r=0.970-0.990$) and sweet potato cultivars ($r=0.937$) (Teow et al., 2007; Stintzing et al., 2005). These high correlations result from the contribution that the main phenolic compounds of potato tubers make to their hydrophilic antioxidant capacity. Additionally, phenolic compounds can transfer an oxygen molecule to the peroxy radical, which is the basis of the peroxy radical reaction evaluated in the ORAC assay, which involves a hydrogen atom transfer mechanism (Andre et al., 2009). Therefore the TPC can be used as an indicator in assessing the AA of fruits and vegetables, including the tubers of potato cultivars.

4.3.7 Principal component analysis

PCA revealed that 14 principal components (PC1–PC14) explained the variance among the data, with the first two PCs explaining 56.84% of the total variance (Figure 4.1). PC1 explained 38.31% and PC2 explained 18.53% of the total variance, which indicated that the first two PCs concerned variables that differentiated the studied cultivars. TS, DM, RS and the textural parameters shear force (She), hardness (Har), chewiness (Che) and cohesiveness (Coh) had positive loadings and AA, TPC, reducing sugar, total acid and the colour parameter hue angle had negative loadings for PC1. AA, DM and Har had negative loadings and the other properties shown in Figure 4.1 had positive loadings for PC2.

The scores of the eight potato cultivars for the first and second PCs are shown in Figure 4.2. The distribution of the cultivars along PC1 reflected their DM, TS, She and Har. Tubers of the Spirit, Kennebec, Cherie and Caesar cultivars had positive scores for PC1, indicating their higher DM, TS, She and Har values. In contrast, tubers of the Agata, Agria and Monalisa cultivars, which had negative scores for PC1, had higher AA and reducing sugar content. Furthermore, the distribution of the cultivars along PC2 reflected their hue angle, springiness (Spr), Coh and Che. Regarding the first and second PCs, the Spirit cultivar had higher positive scores for both, which indicated that this cultivar had higher DM, TS, She, Har, Spr, Coh, Che and hue angle values than the other cultivars tested.

According to the PCA, the eight commercial potato cultivars were classified into three groups: the Cherie, Kennebec, Agria, Caesar and Red Pontiac cultivars in group 1, the Agata and Monalisa cultivars in group 2 and the Spirit cultivar in group 3. The physical and chemical properties of the different cultivar groups were distinct: the group 1 cultivars had higher DM, TS, shear force and hardness; the group 2 cultivars had higher AA, reducing sugar content, hue angle, springiness, cohesiveness and chewiness; the group 3 cultivar had higher DM, TS, shear force, hardness, springiness, cohesiveness, chewiness and hue angle. Certain nutritional and functional parameters of the different cultivar groups indicated the potential efficacy of different cultivars to satisfy the nutritional needs of consumers and industrial use. The group 1 and group 3 cultivars were suitable for frying because of their higher DM and lower reducing sugar content, enabling one to obtain a less coloured product and low levels of acrylamide content, which was attributed to Maillard reactions (Muttucumaru et al., 2014). The group 2 cultivars were fit for boiling and baking because of their higher values of springiness, cohesiveness and chewiness, and not peeling the cultivars before boiling and baking may increase their antioxidant properties and thus health benefits (Reyes et al., 2005). The textural attributes are important for describing the variation between the analysed cultivars. Hardness could indicate the aptitude use of potato cultivars. Kreutzmann et al. (2011) found that the frying potato cultivars with higher mealiness significantly and positively correlated with hardness; the boiling and baking potato tubers

with lower mealiness had higher scores. As Figure 4.2 showed, the group 1 and group 3 cultivars had higher hardness than the group 2 cultivars, which also proved that the group 1 and group 3 cultivars were fit for frying and the group 2 cultivars for boiling and baking. In general, our study showed that the physicochemical properties analysed enable to classify potato cultivars and predict their aptitude use.

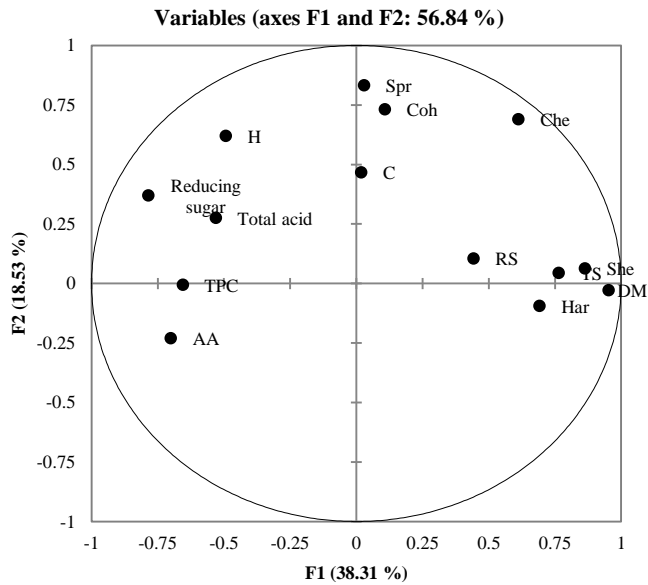


Figure 4.1 Loadings of the physicochemical properties on the first and second principal component (PC). DM=dry matter, TS=total starch, RS=resistant starch, TPC=total phenolic content, AA=antioxidant activity, C=chroma, H=hue angle, She=shear force, Har=hardness, Spr=Springiness, Coh=cohesiveness, Che=chewiness

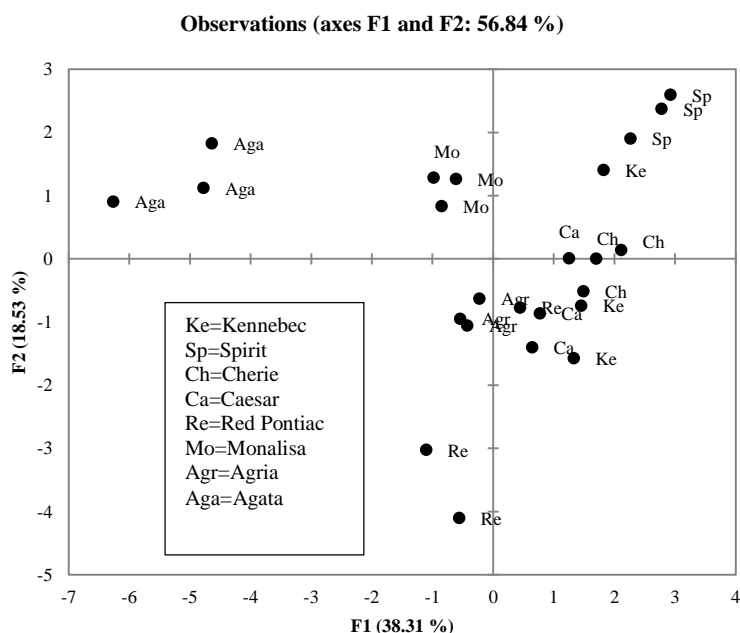


Figure 4.2 First and second principal-component scores of the potato cultivars

4.4 Conclusions

A statistical study of correlations between all parameters analysed was conducted to discover associations between measured pairs of these parameters. Significant ($P < 0.05$) and positive correlations were found due to the common and complex interactions. It is recommended that the potato skin not be removed during the cooking process (boiling or baking) due to its higher TPC and AA. The organic acid content was similar to that previously reported, but lactic acid was present in all cultivars studied.

The PCA results classified the eight cultivars studied into three groups: (1) Cherie, Kennebec, Agria, Caesar and Red Pontiac; (2) Agata and Monalisa; (3) Spirit. The physical and chemical properties of the three cultivar groups were notably different, which determined the aptitude of the potato cultivars for processing. The group 1 and group 3 cultivars were suitable for frying owing to their higher hardness and DM content and lower

reducing sugar content, while the group 2 cultivars were fit for boiling and baking because of their higher values of springiness, cohesiveness and chewiness, and not peeling the cultivars increased their antioxidant properties. These properties and groups may explain and reinforce the cooking types of the cultivars proposed by the European Cultivated Potato database.

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Chapter 5

Effect of the intensity of cooking methods on nutritional and physical properties of potato tubers

This chapter has been submitted as:

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Abstract

The different intensities of common culinary techniques (boiling, baking and microwaving) produce several changes that reduce the nutritional and physical properties of potatoes. This study evaluated the effect of those cooking methods on the quality of commercial potato tubers (Agata, Kennebec, Caesar and Red Pontiac). The higher weight losses were obtained for baking, but the potato softening depended on the cultivar. Color losses were independent of the intensity of the treatment; however, microwaving promoted a prompt starch gelatinization with respect to the other methods. The resistant starch retention of baking and microwaving was higher than that of boiling, and the maximum retention of bioactive compounds was obtained with the lower core temperature during boiling, as well as higher temperature and shorter baking time and the lower power and longer microwaving time. Principal component analysis revealed significant relationships between the instrumental and functional properties of cooked potatoes.

Keywords: boiling; baking; microwaving; resistant starch; antioxidant activity; texture

5.1 Introduction

Potatoes (*Solanum tuberosum* L.) are an important source of carbohydrates and are consumed widely in the developing world and in the developed world (Bordoloi et al., 2012). The potato tubers are commonly cooked before consumption, and the traditional and most popular cooking methods include boiling, frying and baking. It is well known that cooking treatments induce significant changes in the physical and chemical compositions to influence the concentration and bioavailability of bioactive compounds in potato tubers (Spanos et al., 1990; Price et al., 1997). However, both positive and negative effects have been reported depending on the differences in the process conditions and in the morphological and nutritional characteristics of potato samples (Liu et al., 2007).

Heat-treatment is a complex process that involves many physical, chemical and biochemical changes in food. In particular, during potato cooking, starch gelatinization occurs, which affects the palatability, digestibility and causes softening of the raw starch matrix. Heat is transferred into the potato tubers primarily by convection from the heating media (water) (Barba et al., 2008). Different cooking conditions have significantly different effects on the properties of potato tubers.

The physical properties of potatoes are greatly affected by the heat treatments. Texture and color are considered very important parameters in the cooking quality of potato samples, and they may influence consumer purchase of these potato products (Waldron et al., 1997; Turkmen et al., 2006). Changes in the texture are usually dramatic, which is due to the membrane disruption and the associated loss of turgor (Waldron et al., 1997). The texture of cooked potato has also been associated with dry matter, sugars, etc. Many attempts have been made to determine the relationship between the texture of cooked potato and the physical or chemical properties of potato starch (Kaur et al., 2002). Other changes in the potato tuber microstructure and texture during cooking have been mainly associated with the gelatinization behavior of starch through the cell wall, and the middle lamellae structural components also play a role (Alvarez et al., 2001). Additionally, cooked potatoes usually exhibit poor color quality compared with fresh tubers because of browning (Turkmen et al., 2006).

The cooking treatment leads to an increase in the rate of starch hydrolysis by gelatinizing the starch and making it more easily available for enzymatic attack during digestion (Bordoloi et al., 2012). Mulinacci et al. (2008) reported that microwaving tends to reduce the starch availability for digestive enzymes, as shown by hydrolysis curves that are consistently lower than those obtained for boiled potatoes. This finding is observed because the crystallinity of potato starch increases during microwave irradiation, and boiling tends to destroy the crystalline structure. The starch molecules undergo several physical modifications depending upon the type of starch, and the severity of the conditions applied affected the content of resistant starch (Yadav, 2011). The resistant starch (RS) content and

the effects of different cooking methods on the RS content have been on studied by several researchers (Mulinacci et al., 2008; Yadav, 2011). However, the results regarding the effect on the RS conflicted.

Apart from being a rich source of starch, potatoes contain small molecules and secondary metabolites that play an important role in many treatments (Friedman, 1997). Potatoes are good sources of natural antioxidants, such as vitamins, carotenoids, flavonoids and phenolic compounds. These natural antioxidants show potential actions against the risk of several age-related diseases, such as cancer, cardiovascular disease, cataract and macular degeneration (Chuah et al., 2008). Although the phenolic content has been extensively studied for raw potatoes (Al-Saikhan et al., 1995; Reyes et al., 2005; Stushnoff et al., 2008; Rumbaoa et al., 2009), there have been many discrepancies regarding the effect of heat treatments on the phenolics and antioxidant activity of potato samples, which could be due to the different processing conditions. Some literature has suggested that a shorter cooking time and lower temperature increased or did not change the total phenolic content and the antioxidant capacity (Navarre et al., 2010; Perla et al., 2012; Blessington et al., 2010; Lachman et al., 2013; Dao, & Friedman, 1992; Mulinacci et al., 2008).

Although there is some previous research on the effect of potato processing, very little information is available on the main components and the bioactive compounds. Thus, it is critical to understand the effect of such processing techniques on the activity and composition and physiochemical properties of potatoes. Therefore, we evaluated the effect of temperature and time of culinary treatments (boiling, baking and microwaving) on the nutritional components and physical properties of commercial potato tubers. The relationships between the different cooking treatments and the potato properties necessary for obtaining higher quality cooked potato products were also assessed.

5.2 Materials and Methods

5.2.1 Potato samples

Potato tubers (*Solanum tuberosum* L.) from four potato cultivars that are grown and consumed worldwide (Agata, Caesar, Kennebec and Red Pontiac) were selected according to the classifications of chapter 4 (Caesar, Kennebec and Red Pontiac belonged to the group 1; Agata belonged to group 2) and their cooking type which is defined by the European Cultivated Potato database (www.europotato.org, 2015), and they were obtained from Mercabarna (Mercados de Abastecimientos de Barcelona S.A., Barcelona, Spain). All of the potatoes were grown in Europe and had the same post-harvest storage conditions. The color of the flesh of the tubers was light-yellow, except for the Kennebec cultivar, which was white. The color of the skin was white-yellow, except for Red Pontiac, which was red.

5.2.2 Samples preparation

The average weight of the potato tubers ranged from 175.09 to 337.60 g. Approximately 18 kg of each potato cultivar of a similar size and weight were selected, washed with tap water and dried on paper towels. The potatoes were cooked with the peels. In this study, three cooking methods, boiling, baking and microwaving, at two different intensities (time-temperature) were evaluated in the four cultivars selected (Table 5.1). Each individual experiment was conducted in triplicate. The cooking conditions were determined in a preliminary experiment for each heat treatment (data not shown). To acquire the experiment data and to validate the heat transfer model, copper–constantan thermocouples (TC Direct, Spain) were used to measure the temperature during the heat treatments.

The cooking value, C_{100} , relates the quality loss during a high-temperature thermal process to an equivalent cooking process at 100 °C (Lund, 1977), and the value was estimated using the equation

$$C = \int_0^t 10^{\left[\frac{T-T_{ref}}{z_Q}\right]} dt \quad (1)$$

Where Z_Q (Z-value) and T_{ref} (reference temperature) represent the most heat-labile component. Generally, the reference cooking value is characterized by $Z_Q = 33.1$ °C and $T_{ref} = 100$ °C (Ling et al., 2015).

After processing, the cooked potatoes cooled for 1 h and were analyzed. A portion of the samples were lyophilized using a freeze-drying instrument, Cryodos-45 (Terrasa, Spain), packed in plastic bags and maintained at -20 °C until further use.

Table 5.1 Description the conditions of different culinary treatments

Heat-treatment	Temperature/Power	Time (min)
Boiling (Bo _{100/50})	100 °C	50
Boiling (Bo _{100/60})	100 °C	60
Baking (Ba _{250/60})	250 °C	60
Baking (Ba _{220/65})	220 °C	65
Microwaving (M _{700/25})	700 W	25
Microwaving (M _{560/35})	560 W	35

Boiling: potato: water = 1:3; cooked in the covered pan using the magnetic induction heating; the time was from the start point.

Baking: cooked in a domestic hot-air oven.

Microwaving: cooked in a domestic microwave oven.

All the experiments were conducted in triplicate.

5.2.3 Physical properties analysis

Weight loss and dry matter

The weight loss was expressed by the ratio of weight difference between the fresh and processed samples to the original weight. The dry matter was analyzed following the gravimetric method (AOAC 931.04). Briefly, 3 g of ground potato samples were dried at 65 °C until they were a constant weight. The dry matter content was calculated as $g \cdot kg^{-1}$. The analyses were conducted in triplicate, and the results are expressed as the mean values \pm standard deviation.

Texture: Shear force and texture profile analysis (TPA)

The shear force of the potato tissues was measured using the texture analyzer (TAXT plus, Stable Microsystems, Surrey, UK), as described by Singh et al. (2008). The potato samples were hand-peeled and then cut into strips (1×1×6 mm) with a stainless steel slicer. The test conditions used for the measurement included a speed of 1 mm/s and a target distance of 22 mm. The shear force was taken as the area under the curve (N). Six potato strips were used for each sample, and the results are expressed as the mean value ± standard deviation. The cooking degree was calculated by the ratio of the final shear force to the original shear force as a measure for the degree of cooking in the potatoes (Bourne, 1989).

The texture profile analysis (TPA) was performed with a 75 mm diameter cylinder probe. The potato cylindrical samples were obtained using a plastic cork broker with a diameter of approximately 19.0 mm. Each cylinder was subsequently trimmed to a length of 10.0 mm using a mechanically guided razor blade. The following parameters were set: a test speed of 0.83 mm/s and a rest period of 5 s between the two cycles. The maximum extent of deformation was 40% of the original length (Alvarez et al., 2001). According to the definitions of Szczesniak (1975) and Bourne (1978), the TPA values for hardness (N), cohesiveness (dimensionless), springiness (mm) and chewiness (N x mm) were calculated from the resulting force-time curve. Six potato cylinders were tested for each potato sample, and the results are expressed as the mean value ± standard deviation.

Color

The color of the potato samples was measured with a MINOLTA tristimulus colorimeter, CR-400 model (Minolta camera, Osaka, Japan), in the CIE lab space. The L* (lightness), a* (greenness [-] to redness [+]), b* (blueness [-] to yellowness [+]), C (Chroma, 0 at the center of the color sphere) and H° (Hue angle, red=0°, yellow=90°, green=180°, blue=270°) were recorded, and three different positions were evaluated. The parameters of hue angle (H°) and chroma (C) were calculated using: $H^\circ = \tan^{-1}(b^*/a^*)$ and $C = (a^{*2} + b^{*2})^{1/2}$. Six measurements

were performed for each potato sample, and the results are expressed as the mean value \pm standard deviation.

5.2.4 Chemical compounds analysis

Starch profile

The total starch (TS) and resistant starch (RS) contents were analyzed through their enzymatic hydrolysis to D-glucose using the AOAC 996.11 (amyloglucosidase/ α -amylase method) and AOAC 2002.02 methods, respectively (Megazyme, Ireland). D-(+)-Glucose obtained was oxidized to D-gluconate, which was quantitatively measured by the absorbance at 510 nm. TS and RS content were calculated as glucose \times 0.9. The results were expressed as g \cdot kg⁻¹ of the lyophilized weight (LW). Each sample was analyzed in triplicate.

Extraction process for determination of sugars, total phenolic and antioxidant capacity

Methanol extracts were obtained according to Andre et al. (2009) with slight modifications. Briefly, the lyophilized powder of each sample was mixed, and 1 ± 0.01 g was weighed. The solid-liquid extraction was performed using acidified methanol/water (80:20 v/v) via sonication (Bandeline Sonoplus GM70, Germany) in ice bath and centrifugation (Selecta, Medifriger-BL, Spain) at 4500 rpm at 4 °C. The supernatant was filtered through Whatman No.1 filter paper, and the pellet was re-extracted as before. The extracts were mixed and evaporated to dryness in a rotary evaporator at 40 °C (Laborata 4000 Efficient, Germany). The concentrate was acidified and stored at -20 °C until further analysis. All samples were extracted in triplicate.

Sugars

The sugar contents were analyzed using a high-performance liquid chromatography HP1100 (Hewlett-Packard, Waldbronn, Germany) equipped with a Beckman 110B injector and a Beckman Refraction Index Detector (Beckman Instruments, Inc., San Ramon, CA, USA).

The separation was performed using a Phenomenex Lunacolumn (250 x 4.6 mm i.d.), following the method of Rodriguez-Galdon et al. (2010). The liquid extracts were filtered through a 0.45 μm membrane filter before injection. The mobile phase consisted of acetonitrile/water (75:25, v/v), and the flow rate was 1.4 $\text{mL}\cdot\text{min}^{-1}$. Individual sugars (glucose, fructose and sucrose) were identified and quantified. Each extract was analyzed in triplicate, and the results are expressed as $\text{g}\cdot\text{kg}^{-1}$ of LW.

Total Phenolic content

The total phenolic content (TPC) of potato skin and flesh extracts was assessed using a modified version of the Folin-Ciocalteu assay (Singleton et al., 1999). The absorbance was measured at 765 nm by a spectrophotometer (Thermo electron Corporation, UK). Each extract was analyzed in triplicate, and the results are expressed in g of Gallic acid equivalent $\cdot\text{kg}^{-1}$ LW (g GAE $\cdot\text{kg}^{-1}$ LW).

Antioxidant activity

The antioxidant activity (AA) of the extracts of the potato flesh and skin was performed using the oxygen radical absorbance capacity (ORAC) assay, as described by Gorjanovic et al. (2013). Approximately 15 μL of diluted sample or standard solutions (Trolox) was mixed with 150 μL of 9.57×10^{-2} μM fluorescein in a well plate. The plate was incubated at 37 $^{\circ}\text{C}$ for 10 min. The reactions were initiated by the addition of 50 μL of AAPH (2, 2- azobis (2-amidinopropane) dihydrochloride) solutions. The fluorescence was measured every 2 min for 120 min at 37 $^{\circ}\text{C}$ using emission and excitation wavelengths of 485 and 530 nm, respectively, using a microplate fluorescence reader (SynergyTM Multi-detection Microplate Reader, BIO-TEK Instruments, USA) until the decay of the kinetic curve was complete. The area under the curve (AUC) was calculated for each sample and standard. The reagents, standard and samples were prepared with phosphate buffer at a pH of 7.40. The results are expressed by g of Trolox equivalents (TE) per kg^{-1} of LW. Each extract was analyzed in triplicate.

5.2.5 Statistics

All of the experiments were conducted in triplicate. The variation between the content of the potato components was evaluated using one-way analysis of variance (ANOVA) with Minitab 17 Statistical software (MINITAB Inc., State College, PA, USA). The differences between the mean values were evaluated using the HSD Tukey test with a 95% confidence interval. A principal component analysis (PCA) was conducted to illustrate the relationship between the variables and analyzed using STAT-ITCF statistical software (Bordeaux, France).

5.3 Results and discussion

5.3.1 Time-temperature profiles and cooking value of the heat-treatments

The starch gelatinization in potato tubers is dependent on the temperature evolution during the cooking process. Alvarez et al. (2001) studied the cooking of potatoes and found that at 60 °C the gelatinization process in the samples was very slow. At 70 °C, they found that the starch granule gelatinization was also partial, and between 82 °C and 90 °C, the potato starch completely gelatinized but only for a very short time. In our study, the temperature curves obtained for the different cultivars under the same treatment were very similar. However, the curves for the different cooking conditions were distinct, especially for microwaving, which is significantly different from baking and boiling (Figure 5.1). Additionally, for microwaving, when the power was higher, there was less time needed to achieve the total gelatinization of the starch because of the quick increase in the core temperature. The cooking values (C_{100} , min) for the experiments are shown in Table 5.2. According to this parameter, the related intensity of the cooking treatment is higher for microwaving and baking, and followed by boiling. For the microwaving treatment, there were no significant differences between cultivars at the two powers tested ($P < 0.05$).

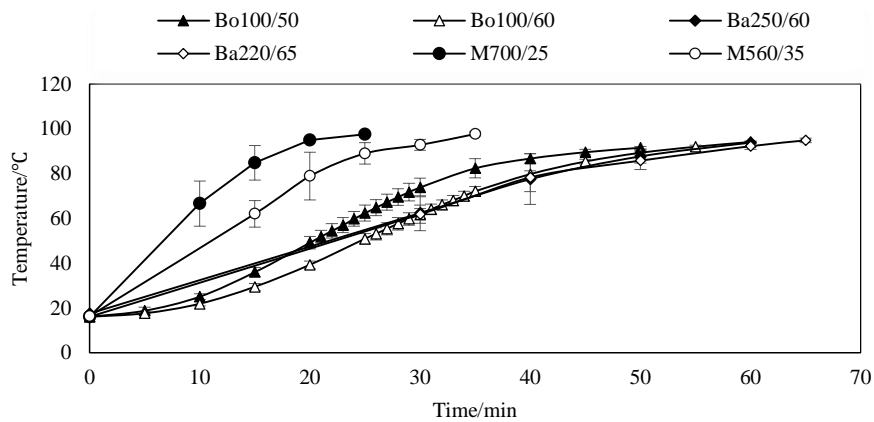


Figure 5.1 Temperature curves of a typical potato cultivar (Kennebec) during Boling, Baking and Microwaving. Values are expressed as average \pm standard deviations (n=3).

Table 5.2 Weight loss (%), cooking degree and cooking value (C100, min) in processed potatoes

Cultivar	Bo100/50	Bo100/60	Ba250/60	Ba220/65	M700/25	M560/35
<i>Weight loss</i>						
Kennebec	0.94±0.10 ^{bC}	0.90±0.02 ^{aC}	19.93±0.06 ^{bA}	21.35±0.05 ^{aA}	11.41±0.08 ^{aB}	11.97±0.08 ^{aB}
Red Pontiac	1.76±0.08 ^{aC}	1.53±0.15 ^{aC}	23.29±0.25 ^{abA}	22.05±0.19 ^{aA}	12.56±0.04 ^{aB}	14.56±0.05 ^{aB}
Caesar	1.53±0.01 ^{abC}	1.65±0.06 ^{aC}	23.63±0.18 ^{abA}	22.24±0.14 ^{aA}	12.42±0.04 ^{aB}	13.57±0.21 ^{aB}
Agata	1.51±0.02 ^{abC}	1.38±0.04 ^{aC}	24.13±0.31 ^{aA}	21.17±0.27 ^{aA}	11.49±0.16 ^{aB}	14.14±0.25 ^{aB}
<i>Cooking degree</i>						
Kennebec	9.76±0.19 ^{aA}	11.09±0.16 ^{aA}	7.30±0.13 ^{aA}	7.03±0.18 ^{abA}	10.53±0.16 ^{bA}	8.36±0.19 ^{bA}
Red Pontiac	7.91±0.18 ^{aB}	8.10±0.16 ^{abB}	5.00±0.14 ^{bB}	8.79±0.14 ^{aB}	18.81±0.15 ^{aA}	18.50±0.12 ^{aA}
Caesar	5.98±0.19 ^{abAB}	7.43±0.22 ^{abA}	4.85±0.14 ^{bB}	5.35±0.15 ^{bcB}	4.93±0.18 ^{cB}	5.75±0.10 ^{bAB}
Agata	3.59±0.23 ^{bB}	4.35±0.28 ^{bB}	3.47±0.18 ^{bB}	4.34±0.14 ^{cB}	5.04±0.24 ^{cAB}	7.21±0.14 ^{bA}
<i>Cooking value</i>						
Kennebec	5.21±0.27 ^{aC}	6.17±0.21 ^{aBC}	10.84±0.13 ^{aA}	6.42±0.25 ^{aBC}	7.72±0.20 ^{aB}	7.34±0.13 ^{aB}
Red Pontiac	4.26±0.13 ^{aC}	4.90±0.18 ^{bC}	6.86±0.24 ^{bAB}	6.38±0.19 ^{aB}	7.08±0.25 ^{aAB}	7.58±0.15 ^{aA}
Caesar	4.11±0.25 ^{aC}	6.06±0.28 ^{aB}	7.75±0.27 ^{bA}	7.15±0.36 ^{aAB}	7.63±0.27 ^{aAB}	8.34±0.29 ^{aA}
Agata	4.53±0.31 ^{aD}	5.68±0.2 ^{abCD}	8.96±0.19 ^{abA}	6.98±0.29 ^{aBC}	8.08±0.28 ^{aAB}	7.96±0.34 ^{aAB}

Values are expressed as average ± standard deviations (n=3).

One-way balance ANOVA by Turkey's test was performed.

Means with different small letters are significant in columns and means with different capitals are significant in rows ($P < 0.05$).

5.3.2 Effect of cooking treatments on physical properties

Weight loss and dry matter content

Depending on the treatment, the weight losses that were obtained were significantly different (Table 5.2). Boiling produced the minimum values for all of the cultivars (< 2%), whereas baking produced the highest losses (>20%). Blaszcak et al. (2004) studied the mechanical properties and microstructure of the potatoes after boiling and microwaving, and they concluded that the weight losses obtained during microwaving (19-23%) were due to the presence of less hydrated and swollen starch granules that promote the evaporation of

cellular water during microwave cooking. For our results, less losses were obtained after microwaving (<15%). In addition to the intensity of the treatment (C₁₀₀, min), the process time plays a key role in the weight loss when there is no water present during the cooking process. The possible differences in the microstructure of the potato peel may affect the water evaporation during the cooking procedures. Figure 5.2 shows the dry matter content of the potato samples. The dry matter content of cv. Kennebec was significantly higher than in the other cultivars. However, the treatments affected the dry matter content of the potatoes in a similar way, which was independent of the initial value. For the four studied cultivars, baking and microwaving led to a higher dry matter content, which is due to the water losses that occur during processing.

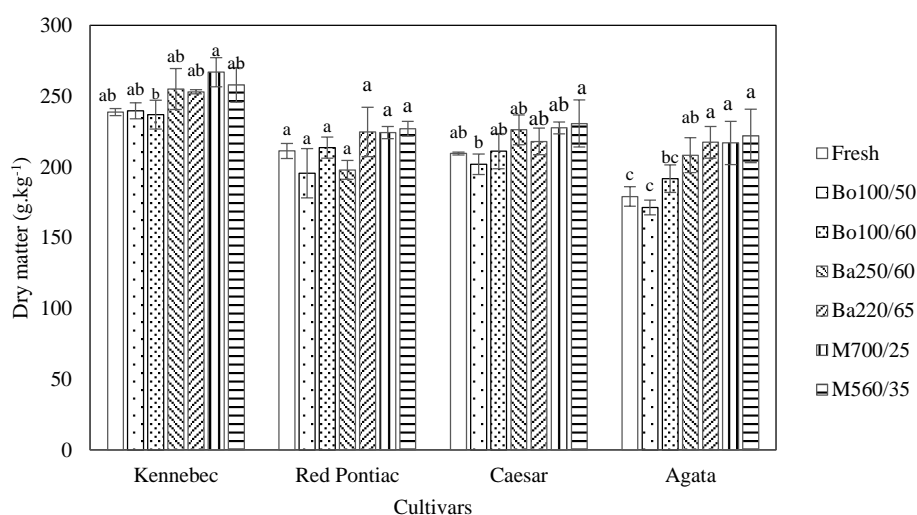


Figure 5.2 Effect of the different cooking treatments on the dry matter content of potato cultivars.

Values are expressed as average \pm standard deviations (n=9).

Means with different small letters are significant ($P < 0.05$) in different treatments at the same cultivars.

Texture parameters

The texture parameters of the fresh and cooked potatoes were evaluated. For the raw potatoes, the shear force of cv. Caesar was significantly higher than for cv. Red Pontiac (Table 5.3). Seefeldt et al. (2011) stated that the changes in potato texture after cooking are related to the physicochemical properties and structure of the cell wall. The texture of cooked potatoes depends on the cooking conditions as a result of various factors, such as starch gelatinization, pectin degradation, cell wall breakdown, cell separation, etc (Nourian et al., 2003). In our study, textural properties were directly affected by the cooking temperature and time. As expected, cooked samples had lower values compared with the raw potatoes. However, the softening of the potato tissues was significantly different between the cultivars. Additionally, when we analyzed the effect of the cooking conditions via the variance of the texture parameters, there were significant differences between the different treatments ($P < 0.05$), as shown in Figure 5.3. The softness of cv. Agata was higher than the other cultivars; moreover, boiling and baking had a higher impact on the hardness and shear force. Hardness can be related to the force that is necessary to break the potato with the incisors during mastication (Garcia-Segovia et al., 2008). For Kennebec, the higher hardness values were due to the higher dry matter content. For that cultivar, the longer boiling period (Bo₆₀) produces less hardness ($P < 0.05$). Alvarez & Carnet. (2001) reported that the harder product may be related to changes in the potato cell wall and middle lamella pectic material that occurs during the heat treatments. After microwaving (M_{700/25} and M_{560/35}), the shear force of cv. Red Pontiac was significantly higher than for the other treatments. Chivarro et al. (2006) suggested that the migration of water from the core of the potatoes slightly lowered the moisture availability in the potato tubers and limited the starch gelatinization. The diffusion of water during the cooking process may be responsible for the differences obtained for the different cooking temperatures (Table 5.2). However, Garcia-Segovia et al. (2008) reported that the texture of cooked potatoes was directly associated with the dry matter content. Our results showed that a significant Pearson correlation coefficient was found between the dry matter and hardness (0.700; $P < 0.001$;

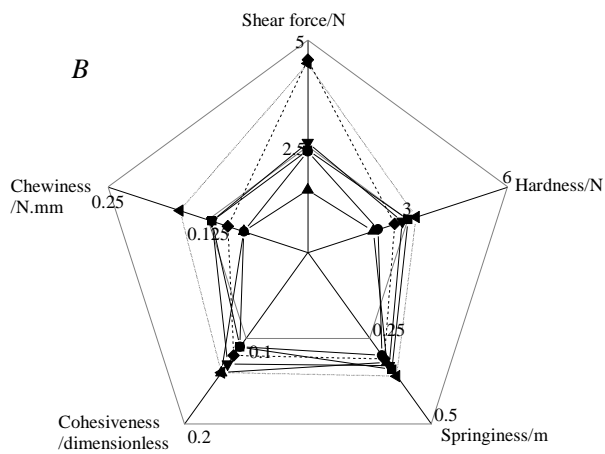
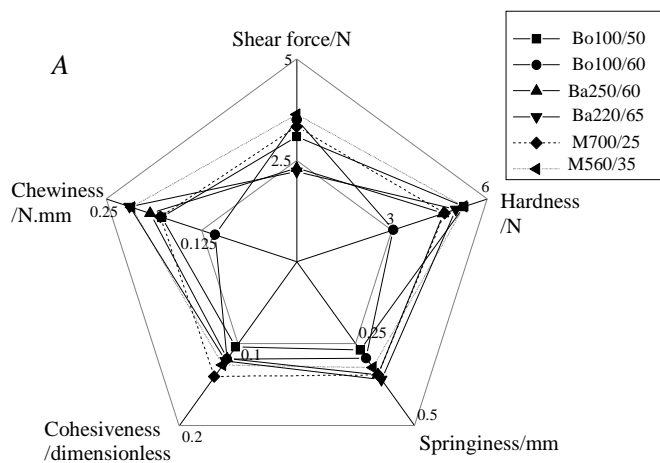
n=74). The analyses of the variance of chewiness and springiness also revealed statistically significant differences between the heat treatments ($P<0.05$). Boiling produced lower chewiness values in all potato cultivars because of the reduced intercellular adhesion that caused breaking of the potato structure (Chiavaro et al., 2006). The cohesiveness differences among the different heat treatments were not significant.

Table 5.3 Textural properties of fresh potato samples

Cultivars	Shear force (N)	Hardness (N)	Textural profile analysis (TPA)		
			Springiness (mm)	Cohesiveness (dimensionless)	Chewiness (N.mm)
Kennebec	31.60±1.61ab	85.01±3.11a	0.50±0.01b	0.38±0.02a	16.37±0.52a
Red Pontiac	29.43±1.11b	98.31±3.79a	0.60±0.02a	0.22±0.02b	12.65±0.62a
Caesar	35.20±1.20a	92.66±3.30a	0.63±0.02a	0.29±0.03ab	16.88±0.68a
Agata	31.31±1.53ab	81.86±2.92a	0.61±0.02a	0.30±0.01ab	15.22±0.55a

Values are expressed as average ± standard deviations of 10 individual potatoes.

One-way balance ANOVA by Turkey's test was performed and the mean values with different small letters are significant in columns ($P<0.05$).



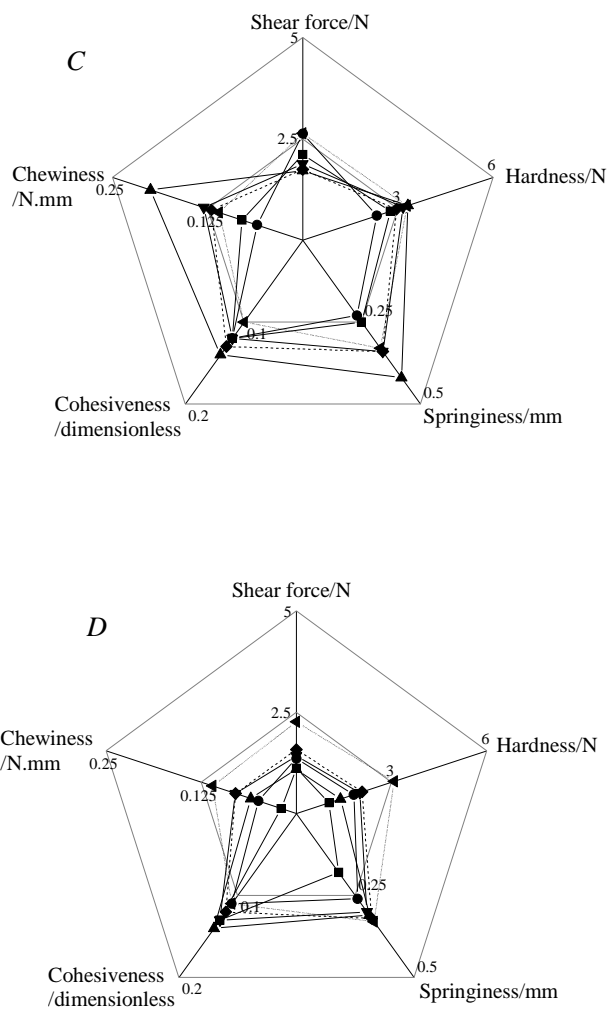


Figure 5.3 Textural analysis parameters for different potato cultivars (A/ Kennebec; B/ Red Pontiac; C/ Caesar; D/ Agata) caused by different cooking treatments.

Values are expressed as average (n=9).

Color

The Lightness (L^*), Chroma (C) and Hue (H) values varied considerably among the different raw potato cultivars (Figure 5.4). The L^* values of fresh potato tubers increased from Agata (light yellow) to Kennebec (white) in the range of 51.14 to 65.50. The Chroma values of the fresh potato cultivars were similar except for Red Pontiac, which had a lower value than the other cultivars ($P<0.05$). The Hue value was higher for Agata (light yellow), followed by Caesar (light yellow) and Red Pontiac (light yellow). The lowest Hue value was obtained for Kennebec (white) among all of the fresh cultivars that we analyzed ($P<0.05$).

After cooking, the L^* values decreased significantly except for Caesar ($P<0.05$), in agreement with a previous study on carrots (Mazzeo et al., 2011), which suggests that as the potato samples became darker, the C values decreased. Additionally, the H values increased after the heat treatments of all of the cultivars in comparison with the raw potato samples (Figure 5.4). After cooking, the darkening of the surface of the potatoes is attributed to a non-enzymatic reaction in which a colored chlorogenic acid-ferric iron complex is formed. Some authors have related the browning appearance to the lightness (L^*) measured on the surface of the potato (Lante & Zocca, 2010). Moreover, surprising results were found for the cv. Agata as compared with the values of different cultivars after the treatments: the L^* values were lower, and the C values were higher because of the lower and higher original value of L^* and C, respectively. Additionally, we found that the intensity of the treatment was not proportional to the color loss. Depending on the original color of the potato, the losses were different depending upon the different cooking treatment.

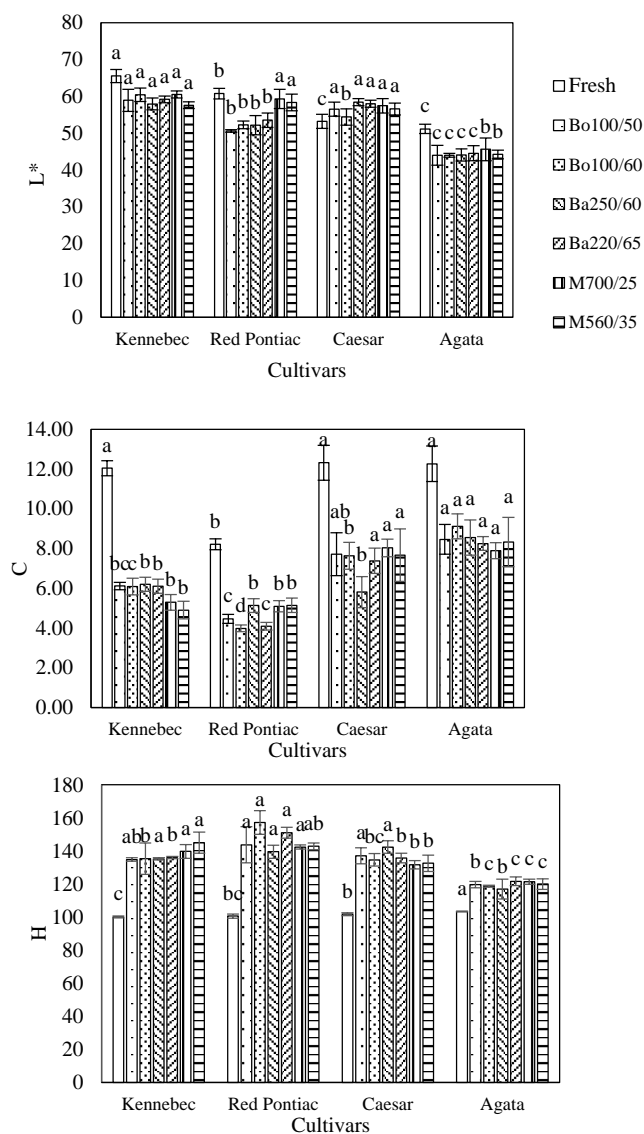


Figure 5.4 Effect of different cooking treatments on the color parameters (L*, C and H) of potato cultivars.

Values are expressed as average \pm standard deviations (n=9).

Means with different small letters are significant ($P < 0.05$) in different cultivars at the same treatments.

5.3.3 Effect of cooking treatments on chemical properties

Starch profiles

The main constituents in potatoes are water and starch. The total starch content varies from 70 to 90% of the dry weight, depending on the botanical variety (Garcia-Alonso & Goni, 2000). The content of total starch (TS) and resistant starch (RS) in fresh potato cultivars ranged from 644.01 to 757.34 g.kg⁻¹ LW and from 467.80 to 599.66 g.kg⁻¹ LW (Red Pontiac<Agata<Kennebec<Caesar), respectively. The cooking treatments produced a new starch profile for all of the cultivars. Generally, the heat produced a significant reduction in the resistant starch (RS) content and an increase in the soluble starch content (Figure 5.5). We observed that the average content of TS slightly decreased during boiling, baking and microwaving in the tested cultivars compared with the original value for the raw potatoes. The baked and microwaved potato samples had lower TS values than the boiled potatoes, possibly due to the difference in the gelatinization during baking and microwaving than during boiling.

When the potato tuber is cooked, almost all of the starch becomes digestible. However, different processing conditions and potato cultivars may affect the final RS content. The highest RS content percentage of the original value of the raw samples for an average of all of the cultivars was found in the baked potatoes. The variation of the average RS values for the potatoes under the different conditions was insignificant. The higher RS content retention in the Kennebec and Agata cultivars was due to the baking treatment, while the higher RS retention of the Red Pontiac and Caesar cultivars was found in the microwaved potatoes. Therefore, the RS content retention for the baked and microwaved potatoes was higher than the retention of the boiled potatoes for all of the tested cultivars, which is in agreement with the report by Garcia-Alonso & Goni (2000). They found that the amount of RS depends on the degree of gelatinization and retrogradation during the cooling of the potato products. A positive and no significant correlation ($r=0.171$, $P=0.152$) was found

between the cooking value and the RS content, which also verified the cooking quality of baking and microwaving over the quality of boiling.

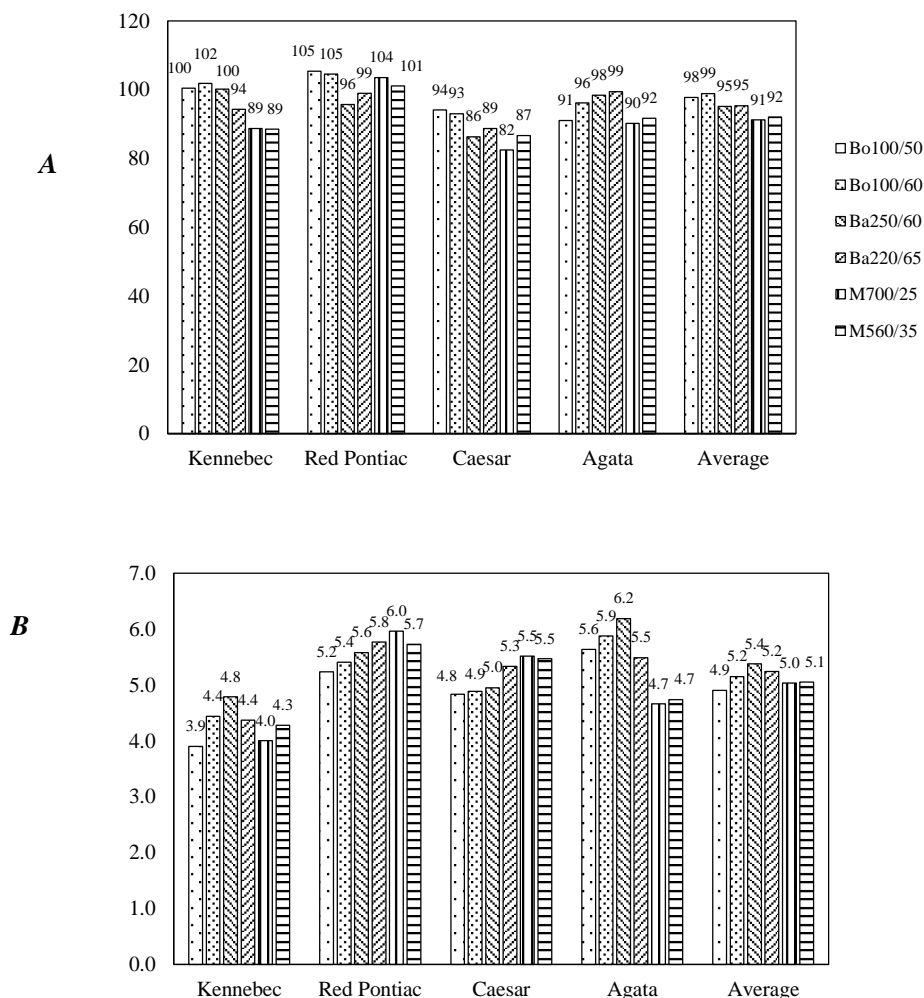


Figure 5.5 Change of the content of starch profiles (A/Total starch; B/Resistant starch) from initial levels in raw potatoes (100%) to final levels (%) caused by boiling, baking and microwaving treatment.

Values are expressed as average (n=9).

Sugars

The sugar content of potatoes is in a form of a reducing monosaccharide, such as D-glucose and D-fructose, and a non-reducing disaccharide, such as sucrose (Lisinska & Leszczynski, 1989). The concentration of glucose (4.66-28.20 g·kg⁻¹ LW) was higher than that of fructose (5.35-25.81 g·kg⁻¹ LW) and sucrose (1.69-6.78 g·kg⁻¹ LW) in all of the fresh potato cultivars, which is in agreement with Plata-Guerrero et al. (2009). The lowest sugar content (fructose, glucose and sucrose) in all of the tested cultivars was cv. Kennebec (Table 5.4). Our results showed that the reducing sugar (glucose and fructose) content of the fresh potato samples ranged from 10.01 to 53.46 g·kg⁻¹ LW, and cv. Red Pontiac and cv. Caesar tubers contained more reducing sugar content than those of the other cultivars ($P<0.05$).

Significant changes in the glucose, fructose and sucrose content were observed during processing as several chemical reactions took place. One of the main reactions is the Maillard reaction in which the glucose and fructose react with amino acids to improve the sensory properties of the product, and the sucrose is hydrolyzed during the heat treatment (Murniece et al., 2011). The free starch can undergo degradation to form a monosaccharide, such as glucose, during processing.

From the results (Table 5.4), we observe that the individual sugars (fructose, glucose and sucrose) increased during baking and microwaving compared with the raw tubers, and the highest increase was due to the baking treatment for all of cultivars, especially baking at 250 °C for 60 min (B_{250/60}). However, the sugar content of certain cultivars decreased during boiling, which may be due to the leaching of sugars in the water during processing. Significant differences between the cultivars were found ($P<0.05$), e.g., the lowest sugar content (fructose, glucose and sucrose) in all of the cultivars after processing was cv. Kennebec due to the low original content.

Table 5.4 Sugars in fresh and processed potatoes ($\text{g}\cdot\text{kg}^{-1}$ LW)

Cultivar	Raw	Bo100/50	Bo100/60	Ba250/60	Ba220/65	M700/25	M560/35
<i>Fructose</i>							
Kennebec	5.35±0.31 ^{c,C}	5.57±0.66 ^{c,BC}	5.74±0.71 ^{b,ABC}	6.98±0.58 ^{b,AB}	7.01±0.42 ^{b,A}	6.42±0.27 ^{b,ABC}	5.62±0.29 ^{c,ABC}
Red Pontiac	25.81±0.94 ^{a,AB}	22.58±1.08 ^{a,BC}	19.55±0.74 ^{a,C}	31.40±1.45 ^{a,A}	27.55±0.99 ^{a,AB}	26.97±1.34 ^{a,AB}	27.17±0.61 ^{a,AB}
Caesar	23.67±0.65 ^{b,A}	16.19±0.35 ^{b,B}	15.19±1.07 ^{a,B}	26.09±0.99 ^{a,A}	24.08±1.05 ^{a,A}	27.01±1.09 ^{a,A}	24.86±0.43 ^{ab,A}
Agata	22.55±0.49 ^{b,A}	24.83±0.53 ^{a,A}	22.16±1.38 ^{a,A}	30.86±1.02 ^{a,A}	27.46±1.11 ^{a,A}	27.88±1.05 ^{a,A}	23.61±0.74 ^{b,A}
<i>Glucose</i>							
Kennebec	4.66±0.20 ^{b,B}	6.71±0.09 ^{c,AB}	7.10±0.22 ^{b,A}	7.30±0.39 ^{b,A}	6.39±0.42 ^{b,AB}	7.69±0.44 ^{b,A}	6.41±0.31 ^{b,AB}
Red Pontiac	27.64±1.13 ^{a,BC}	22.73±1.27 ^{ab,CD}	19.43±1.17 ^{ab,D}	38.37±1.07 ^{a,A}	31.35±1.20 ^{a,B}	27.65±1.15 ^{a,BC}	28.01±1.05 ^{a,BC}
Caesar	28.20±0.69 ^{a,B}	17.81±1.16 ^{b,C}	17.87±1.40 ^{ab,C}	31.77±0.82 ^{a,A}	29.22±1.12 ^{a,AB}	29.50±1.27 ^{a,AB}	28.52±1.12 ^{a,AB}
Agata	25.83±1.03 ^{a,A}	28.90±1.12 ^{a,A}	22.91±1.23 ^{a,A}	34.33±1.23 ^{a,A}	27.46±1.07 ^{a,A}	33.26±0.87 ^{a,A}	26.57±1.03 ^{a,A}
<i>Sucrose</i>							
Kennebec	1.69±0.46 ^{b,C}	4.15±0.25 ^{b,AB}	6.01±0.29 ^{a,A}	5.18±0.29 ^{b,AB}	5.07±0.15 ^{a,AB}	3.92±0.19 ^{b,ABC}	3.25±0.12 ^{b,BC}
Red Pontiac	6.78±0.25 ^{a,AB}	5.32±0.42 ^{b,B}	7.33±0.30 ^{a,AB}	11.28±0.33 ^{a,A}	6.22±0.17 ^{a,B}	8.18±0.24 ^{a,AB}	7.77±0.22 ^{a,AB}
Caesar	5.60±0.34 ^{a,BC}	3.66±0.14 ^{b,C}	5.81±0.29 ^{a,B}	5.76±0.36 ^{b,B}	5.97±0.39 ^{a,AB}	7.21±0.26 ^{a,AB}	8.04±0.25 ^{a,A}
Agata	5.35±0.34 ^{a,B}	9.10±0.45 ^{a,A}	5.29±0.24 ^{a,B}	9.65±0.43 ^{a,A}	8.18±0.35 ^{a,AB}	8.64±0.24 ^{a,AB}	7.29±0.53 ^{a,AB}

Values are expressed as average \pm standard deviations (n=9).

One-way balance ANOVA by Turkey's test was performed.

Means with different small letters are significant in columns and means with different capitals are significant in rows ($P<0.05$).

Total phenolic content

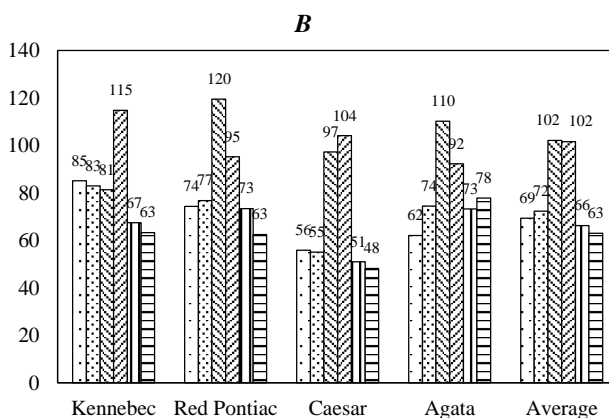
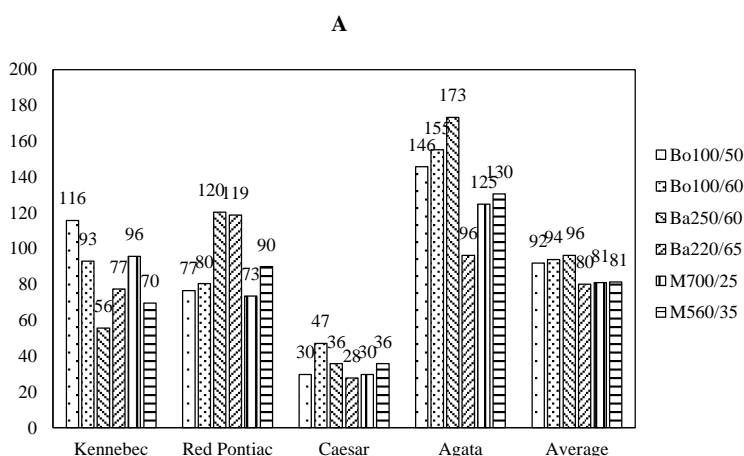
The total phenolic content (TPC) of the fresh potatoes was analyzed for the four cultivars. The evaluation of the fresh potatoes for TPC revealed that there was a higher phenolic concentration in the skin than in the flesh, and it was often two-times more. The TPC of the

potato flesh and skin ranged from 1.05 (Agata) to 2.49 (Caesar) g GAE·kg⁻¹ LW and from 2.89 (Kennebec) to 4.40 (Red Pontiac) g GAE·kg⁻¹ LW, respectively. The TPC of the skin of the cv. Red Pontiac was higher than for the other cultivars because of its red skin color.

Several authors have described a considerable reduction in the amount of TPC during cooking, depending on the cultivar and cooking methods (Perla et al., 2012; Blessington et al., 2010). We observed that the changes in the TPC of the potato flesh were more dependent on the genotype of each cultivar (Figure 5.6A). After cooking, the TPC of cv. Caesar and cv. Agata significantly differed from the other cultivars because of their lowest and highest retentions of TPC, respectively. For the boiling treatment, the TPC retention of Bo_{100/60} in the three cultivars (Red Pontiac, Caesar and Agata) were slightly higher than the content after Bo_{100/50}, which suggests that the lower core temperature assisted in retaining the TPC. The TPC retention percentage after baking, Ba_{250/60}, was higher than Ba_{220/65} in all of the tested cultivars except for Kennebec. For the baked potatoes, the highest temperature and the shortest time retained higher levels of TPC in all three of the potato cultivars. Navarre et al. (2010) stated that baking at 375 °C for 30 min increases the amount of extractable phenolics, while Perla et al. (2012) found a 54.0% loss in the TPC after baking at 204 °C for 60 min. Additionally, the TPC retention values after microwaving, M_{560/35}, were higher than M_{700/25}, which indicates that the lower power plays a key role in retaining a higher TPC content for the microwaved potatoes. In summary, a lower core temperature during boiling, a higher temperature and shorter baking time, and a lower microwave power were all beneficial for retaining the TPC in the potato flesh of the cultivars. Palermo et al. (2014) suggested that the reduction of TPC after the cooking treatments was attributed to water-soluble phenolics that leach into the water (boiling) and breakdown. Therefore, the phenolic compounds are highly reactive species that undergo several reactions during food processing that are related to the cultivars and cooking conditions.

The removal of the skin before or after cooking is influential in determining the phenolic compounds (Blessington et al., 2010). Recently, there have been some controversial results on the effect of different heat treatments on the TPC levels. Mattila & Hellstrom (2007)

observed that the cooked potato peels exhibited enhanced the TPC levels when compared to uncooked peels. In contrast, Mondy & Gosselin (1988) suggested that during processing the phenolic compounds migrated from the peel into both the cortex and the internal tissues of the potato tubers, leading to the decrease in the peel content. Our results suggest that higher losses of TPC in the potato skin were obtained after boiling and microwaving; however, the TPC slightly increased after baking for all of the cultivars (Figure 5.6B).



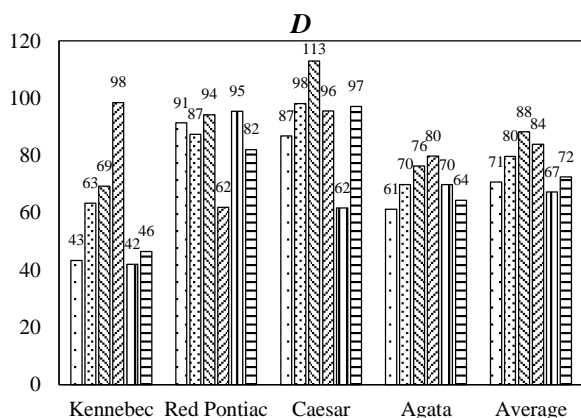
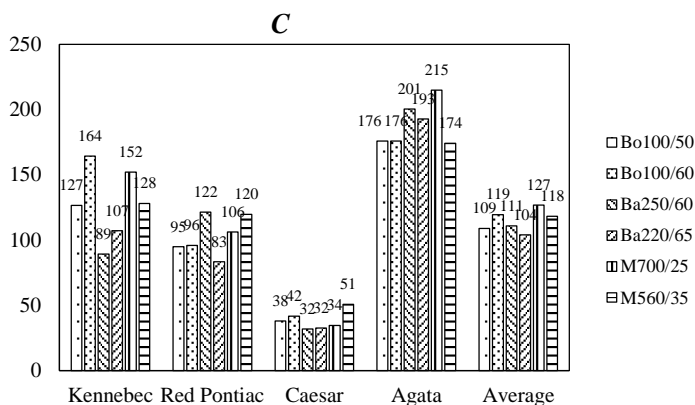


Figure 5.6 Change of the flesh and skin content of total phenolic content (TPC) (A/TPC-Flesh; B/TPC-Skin) and antioxidant activity (AA) (C/AA-Flesh; D/AA-Skin) from initial levels in raw potatoes (100%) to final levels (%) caused by boiling, baking and microwaving. Values are expressed as average (n=9).

Antioxidant activity

The different heat treatments reduced or, in some cases, enhanced the antioxidant activity (AA) of the potato genotypes with respect to the uncooked potato samples (Navarre et al., 2010; Perla et al., 2012; Blessington et al., 2010). The AA in the flesh of the raw potato samples ranged from 9.93 (Agata) to 26.46 (Caesar) g TE·kg⁻¹ LW, and the AA in the skin of the raw potatoes ranged from 60.59 (Caesar) to 97.56 (Agata) g TE·kg⁻¹ LW.

The average AA content in the flesh samples increased due to all of the cooking methods when compared with the uncooked potato samples, which is in agreement with Blessington et al. (2010) & Navarre et al. (2010). However, the largest increase was caused by the microwave treatment. The AA increase in potato flesh may be associated with an increase in the extractability of these compounds from the cellular matrix due to the starch textural changes during the cooking processes (Blessington et al., 2010). Additionally, cooking may result in higher recoveries and produce inactivating enzymes that consume the AA during the processing (Navarre et al., 2010). Although a consistent trend for the AA in the overall average results for all of the cultivars was found, the differences between the cultivars and the heat treatments were inconclusive due to the large internal variability of the cultivars and the different cooking conditions. The cultivars exhibited a more considerable influence on the AA changes in the flesh of the potato samples (Figure 5.6C). The cv. Agata showed a significant increase in the AA of the flesh samples (increased to 174%~215% of the original value). In contrast, the cv. Caesar showed a significant reduction in the AA (to 38%~51% of original value) when compared with the other cultivars.

Potato tubers are always cooked before consumption; however, there is very limited information on the effect of cooking on the AA of cultivars in the flesh and skin, especially in the skin. All of the cooking methods demonstrated a reduced AA in the potato peels in comparison with the uncooked potato peels (Figure 5.6D). The most favorable influence on the content of AA in the peels was achieved via baking, except for with the Red Pontiac at Ba_{250/60}. If potatoes are eaten with their skin, some nutrient losses are avoided.

5.3.4 Principal component analysis

Principle component analysis (PCA) was used to summarize the relationship between the properties of the potato cultivars that were tested after cooking with the different heat treatments. The PCA reduced the number of variables in the physical and chemical properties of the potatoes to simplify the data without loss of relevant information and to improve the understanding of the associations via identification of new, uncorrelated variables (Alvarez & Canet, 2001).

The PCA revealed that fifteen principle components (F1 to F15) explained the variance among the data, and the first two principle components accounted for 77.32% of the total variation (Figure 5.7). The first component (F1) explained 50.83% of the total variance, and the second component (F2) accounted for 26.49% of the total variance, which indicated that the first two principal components included variables that differentiated the tested cultivars. The texture parameters (shear force, hardness and chewiness), color parameters (hue angle and lightness) and cooking degrees had positive loadings, and the RS, AA and Chroma had negative loadings for the first principal component. The weight loss, springiness, cohesiveness and DM had negative loadings, while the TS and TPC had positive loadings for the second principal component. The properties of the potatoes showed similar directions, indicating a strong relationship between these attributes.

After six different processing treatments, four cultivars were scattered, and different groups were observed for the F1 and F2 and are shown in Figure 5.8. However, the scores of samples after microwaving, except for the Kennebec cultivar, are not shown in Figure 5.8 because the scores of the vectors were too close to the zero line. The directions of F1 explained the effect of the cultivars on the properties of the potatoes, whereas F2 explained the effect of the heat treatments on the properties. Regarding F2 for the tested cultivars after different heat treatments, after boiling, all of the tested cultivars were associated with the highest TS and TPC. After baking, the tubers exhibited higher DM, springiness, cohesiveness and weight loss. However, the cultivars that were microwaved could be

classified into two groups: 1) the Kennebec and Red Pontiac cultivars exhibited the highest shear force, hardness, chewiness, H, L and cooking degree, 2) the Caesar and Agata cultivar exhibited the highest RS, AA and C. F1 primarily discriminated the cooked potato cultivars: the Agata cultivars from the Kennebec, Red Pontiac and Caesar cultivars, which also proved the classification groups of Chapter 4. After the heat treatments, the Agata cultivar exhibited higher AA, TPC, RS and C, and the other cultivars (Kennebec, Red Pontiac and Caesar) were associated with the higher TS, DM, cooking degree, the textural parameter values and the color parameter (L and H) values.

The PCA was sufficient to prove the effect of the different treatments and the different cultivars on the properties of the potatoes. However, the cultivars with higher color parameter values (L and H) and the cultivars with all of the textural parameters were associated with more DM and TS content, while the cultivars with higher TPC, AA and RS content were related to the higher color parameter value (L). Additionally, the cultivars after boiling exhibited higher TS and TPC, while the tubers after baking showed DM and weight loss. Therefore, the PCA results verified that there were significant relationships between the physical instrumental properties and the functional properties after cooking. According to the PCA, the physical instrumental properties can be considered as an indicator of some of the nutritional and functional properties of cooked potato products, which can establish the nutritional difference and may be useful in industry. Moreover, some of the nutritional and functional parameters of the different cultivars after the treatments demonstrated the potential efficacy of processing potatoes to satisfy the nutritional needs of consumers and the needs of industry.

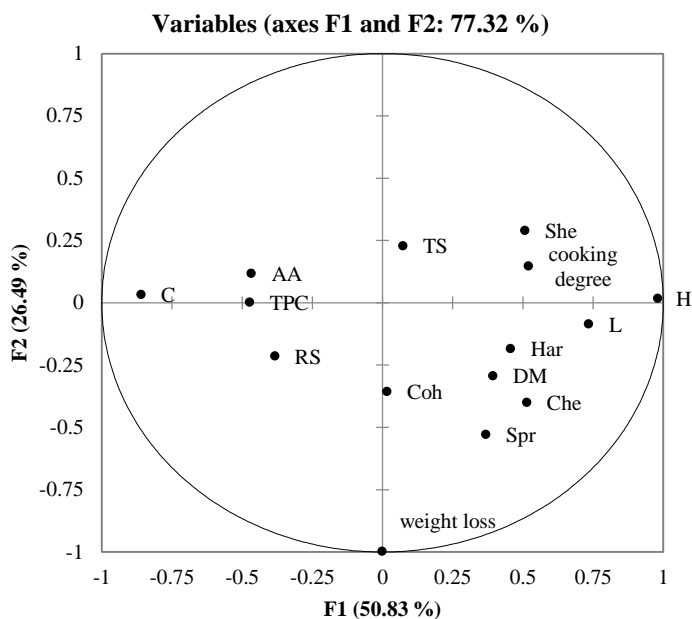


Figure 5.7 Loadings of the physiochemical properties on the first and second principle component (F1 and F2) after the different cooking methods.

DM=dry matter, TS=total starch, RS=resistant starch, TPC=total phenolic content, AA=antioxidant activity, She=shear force, Har=hardness, Spr=springiness, Coh=cohesiveness, Che=chewiness, C=chroma, H=hue angle, L=lightness

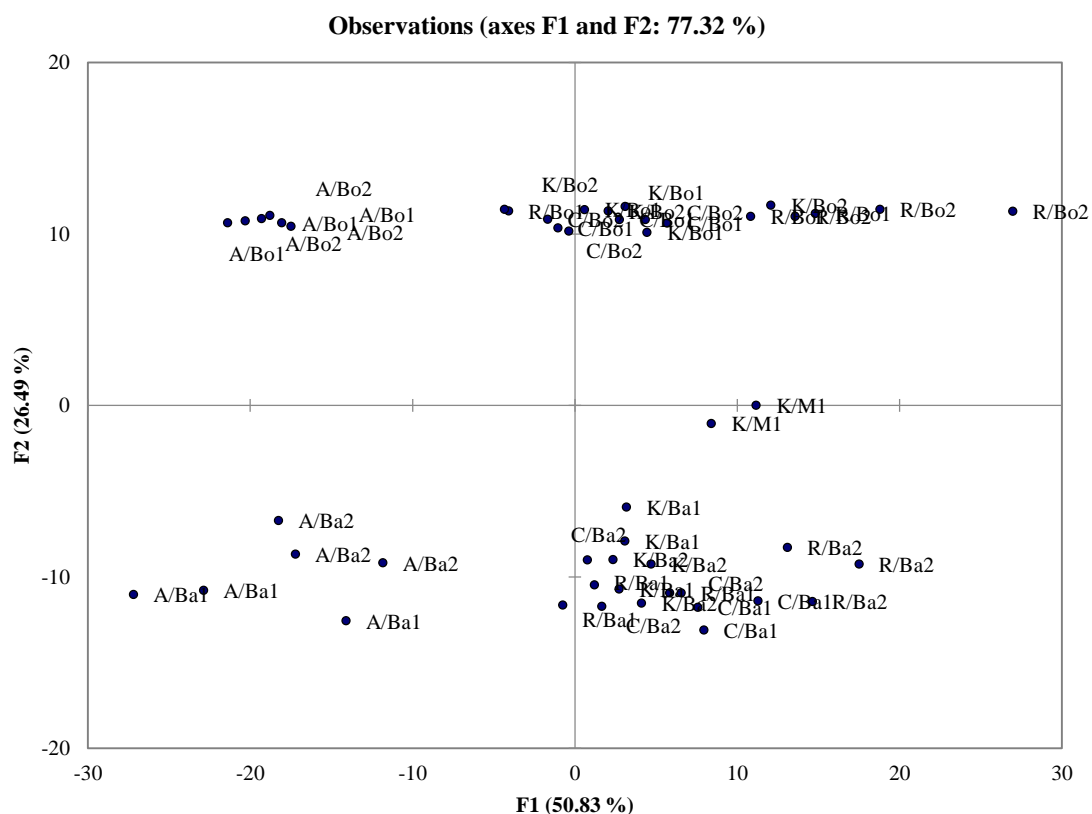


Figure 5.8 First and second principle component scores of the potato cultivars after different cooking methods. The vector values of some microwaving experiments were too closed to the zero line, so some microwaving cultivars had not showed in this figure.

K: Kennebec; R: Red Pontiac; C: Caesar; A: Agata

Bo1: Bo_{100/50}; Bo2: Bo_{100/60}; Ba1: Ba_{250/60}; Ba2: Ba_{220/65}; M1: M_{700/25}; M2: M_{560/35}

5.4 Conclusions

The effect of cooking treatments and cultivars on the physical and chemical properties of potatoes was investigated. Cooking treatments with air involved higher weight losses due to the evaporation of potato water across the skin, independently of the cultivar. Baking was the culinary process that promoted the higher losses. The softening after being cooked was

more dependent on the potato cultivar than heat-treatments. Boiling and baking were the treatments that highly affected the Shear force and Hardness. However, chewiness and springiness were remarkable different between treatments in all tested potato cultivars. The diffusion of water across the potato tissues may be responsible of the differences in softening. All the cooking treatments affected similarly the dry matter of potato independently of the assessed cultivars. Microwaved potatoes had higher values of DM. The intensity of the treatment is not proportional to the color losses after being cooked.

Lesser time is needed for the starch gelatinization of potato during microwaving respect boiling and baking in the studied conditions. The TS and RS decreased after processing and the RS retention of baking and microwaving was higher than that of boiling; the individual sugars (fructose, glucose and sucrose) increased by baking and microwaving, but the content of certain cultivars decreased by boiling.

The effect of the cooking process on the TPC and AA in potato flesh depends on the potato cultivar. However, the maximum retention of bioactive compounds (TPC and AA) was obtained with the lower core temperature during boiling, the higher temperature and shorter time of baking and the lower power of microwaving.

Regarding to the different cultivars and heat-treatments, the PCA results showed that the significant relationships were between the physical instrument properties and functional properties after cooking potato cultivars. PCA results discriminated the Agata cultivars from the Kennebec, Red Pontiac and Caesar cultivars after cooking, which also proved the classification groups of Chapter 4. The physical instrument properties may be considered the indicator of some nutritional and functional properties of cooking potato products, and certain nutritional and functional parameters of different cultivars after treatments indicated the potential efficacy to satisfy the nutritional needs of consumers and industrial use.

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Chapter 6

Influence of the frying process and potato cultivar on acrylamide formation in French fries

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Abstract

Three potato cultivars (Kennebec, Red Pontiac and Agria) commonly used for fried potato products were selected to evaluate the effect of different frying conditions on acrylamide formation in French fries. The main objective was to determine the relationships between the precursors of acrylamide in the fresh potato tubers (reducing sugars and asparagine) and the properties of the fried potato strips (oil uptake, moisture content, colour and texture) with the acrylamide concentration after frying. Frying experiments were conducted at 150, 170 and 190 °C. The potato strips exhibited more acrylamide content, lower oil uptake, higher moisture content, darker colour, and greater hardness when the frying temperature was increased from 150 to 190 °C. Significant positive relationships were observed between the acrylamide level and the asparagine, reducing sugars and sucrose contents, b*, Chroma and shear force and negative correlations with the oil uptake and L* in fried potato strips. In addition, the oil uptake presented significant positive correlations with the L* and H in French fries. However, these relationships were different between individual cultivars, especially for the Agria cultivar, which exhibited no correlation between the studied factors. This study clearly indicates the complex relationship of acrylamide formation with possible precursors in various potato cultivars.

Keywords: reducing sugars; asparagine; colour; texture; oil uptake; sunflower oil

6.1 Introduction

The potato (*Solanum tuberosum*) is one of the world's major agricultural crops and is consumed daily by millions of people from diverse cultural backgrounds (Pedreschi & Moyano, 2005). French fries have been a popular salty snack for 150 years, and their retail sales in the US are almost one-third of the total sales in this market (Garayo & Moreira, 2002).

Frying has been defined as the immersion of a food product in an edible oil above the boiling point of water (Hubbard & Farkas, 1999), with colour, texture and flavour development. It is a complex process because of the two mass transfers in opposite directions within the material being fried; for starchy products, water and some soluble material escapes from the products and oil enters the food (Blumenthal & Stier, 1991). The reports of acrylamide intake indicate that fried potato products, bread and bakery products, coffee and breakfast cereals are the food commodities that contribute the greatest dietary acrylamide exposure (Vinci et al., 2012). EFSA (2011) reported that the 95th percentiles of the acrylamide intake for adults and for children are estimated to range between 0.6-2.3 $\mu\text{g}\cdot\text{kg}^{-1}$ bw/day and 1.5-4.2 $\mu\text{g}\cdot\text{kg}^{-1}$ bw/day, respectively. Acrylamide is a neurotoxin in humans, and it has been considered to be a probable human carcinogen (Hogervorst et al., 2007; Pedreschi et al., 2004). Researchers and industry need to find solutions to reduce or prevent acrylamide formation, despite the lack of legal limits for this contaminant, in foods, especially fried potato products.

Acrylamide is a by-product of the Maillard reaction in food processed at a temperature > 120 °C (Mottram et al., 2002; Stadler et al., 2002). The content of acrylamide is dependent on factors such as the cultivar, fertilization, storage, blanching, cooking temperature and time, and the amount of reducing sugars and free amino acids, such as asparagine, present in the potatoes (Marquez & Anon, 1986; Cheong et al., 2005; Halford et al., 2012). There have been several reports on reducing acrylamide formation, and these strategies were compiled in a “Toolbox” by Food Drink Europe (http://www.fooddrinkeurope.eu/uploads/publications_documents/Toolboxfinal260911.pdf). The reducing sugars and asparagine, as acrylamide precursors, are very important for reducing the acrylamide content in fried potato products (Palazoglu et al., 2010). However, the relationship between the asparagine and reducing sugars concentrations in the fresh potatoes and the acrylamide formation during processing are surprisingly complicated. According to the report of Vinci et al. (2012), asparagine concentrations are relatively high

compared to the reducing sugars content, which represents the limiting factor in acrylamide formation in fried potato products. In contrast, Shepherd et al. (2010) found that the asparagine and sugar concentrations contributed approximately equally to the acrylamide formation. In addition, Halford et al. (2012) suggested that when the sugar concentration was relatively high, acrylamide formation during processing was proportional to the sugar content, whereas when the sugar level was low, acrylamide formation was proportional to the asparagine content.

As one strategy to reduce acrylamide formation, the potato cultivar selection is very important. Some cultivars are more suitable than others for frying in strips, due to their large, long tubers and low reducing sugar content. The frying conditions dramatically affect the levels of acrylamide, as well as the browning, texture, and flavour development caused by the Maillard reaction. The frying time and oil temperature should be controlled to reduce the acrylamide content, and the temperature should not exceed 170-175 °C, as lower temperatures towards the end of the Maillard reaction may reduce acrylamide formation (Vinci et al., 2012). Longer frying periods may result in higher acrylamide contents.

During the frying process, oil is used as the heating medium and as an ingredient producing calorific products. Oil uptake is considered the major nutritional critical point of fried products because of the epidemic obesity prevalent in developed and even in developing countries caused by meals rich in fat (FAO, 2002). In addition, Zamora & Hidalgo (2008) and Capuano et al. (2010) indicated that lipid oxidation positively influences the formation of acrylamide. However, other studies have not discovered any significant negative effect of the oil uptake on acrylamide formation. To date, there is still some confusion and misunderstanding regarding the influence of oil uptake on acrylamide formation. Due to health concerns, consumer preference for low-fat and fat-free products has been the driving force of studies to understand the oil uptake to control and reduce the oil uptake and acrylamide content while still retaining the desirable texture and flavour of fried potato products.

This study aimed to evaluate the influence of frying conditions on acrylamide formation and to investigate the existence of a relationship between acrylamide levels and the factors potentially involved in the formation of acrylamide, such as the frying temperature, reducing sugars, asparagine, moisture, oil uptake and instrumental sensory parameters (colour and texture) in three potato cultivars commonly used for fried products in Europe.

6.2 Materials and Methods

6.2.1 Sample preparation

In accordance with the report by Yang et al. (2015) (Chapter 4), potato tubers (*Solanum tuberosum*) of three cultivars (Red Pontiac, Kennebec and Agria) were selected. Tubers were commercialized in Spain and obtained from Mercabarna (Mercados de Abastecimientos de Barcelona SA, Barcelona, Spain). All potato cultivars were grown in Europe and had the same postharvest storage conditions prior to use. The dry matter content of all potato cultivars was greater than 200 g·kg⁻¹. The flesh colour of the Red Pontiac and Agria cultivars was yellow, and the colour of the cv. Kennebec was white. The mean weights of all the potato cultivars were similar, higher than 200 g. The potatoes were stored at 8 °C and 95% relative humidity and were washed and peeled by hand. The tubers were then cut into strips (1×1×6 mm) with a stainless steel slicer. Sunflower oil containing 65% oleic acid was used in the frying.

6.2.2 Frying conditions

200 g strips of each sample were fried in an electrical fryer (Taurus, Spain) at the following temperature-time conditions: (i) 190 °C for 160 s, (ii) 170 °C for 240 s, (iii) 150 °C for 330 s. The frying period was previously determined by the final colour of the frying strips. The final colour of the fried strips was fixed to standard 3 on the colour scale of the USDA standard for frozen French fries. The potato strips' mass to oil mass ratio (g/g) was 1:5.

Each cultivar was fried in triplicate under the same frying conditions. After frying, portions of the samples were lyophilized using a Cryodos-45 freeze-drying instrument (Terrasa, Spain), packed in plastic bags and maintained at -20 °C until further use.

6.2.3 Instrumental analysis of color and texture

Colour

The colour of the potato strips was measured using a Minolta CR-400 colorimeter (Osaka, Japan) in the CIE lab space. The L* (lightness), a* (greenness [-] to redness [+]), and b* (blueness [-] to yellowness [+]) were recorded and evaluated. The parameters of hue angle (H°) and chroma (C) were calculated as $H^\circ = \tan^{-1}(b^*/a^*)$ and $C = (a^{*2} + b^{*2})^{1/2}$. Six measurements were taken for each experiment, and the results were expressed as the mean value \pm standard deviation.

Texture analysis: Shear force and texture profile analysis

The shear force of the samples was measured using a texture analyser (TAXT plus, Stable Microsystems, Surrey, UK), as described by Singh et al. (2008). The test conditions used for the measurement were pre-test speed 1 mm/s; test speed 1 mm/s; post-test speed 1 mm/s; target distance of 30 mm into the samples and trigger force of 2 g. Six potato strips were taken for each experiment, and the shear force (N) was expressed as the mean value \pm standard deviation.

Each potato strip was cut to a length of 10.0 mm using a knife. The texture profile analysis (TPA) was performed with the parameters set to pre-test speed 0.83 mm/s, test speed 0.83 mm/s and post-test speed 0.83 mm/s; a rest period of 5 s between the two cycles; and a trigger force of 5 g. The maximum extent of the deformation was 10% of the original length. According to the definitions of Szczesniak (1975) and Bourne (1978), the TPA values for hardness (N), cohesiveness (dimensionless), springiness (mm) and chewiness (N x mm)

were calculated from the resulting force-time curve. Six potato strips were tested for each experiment, and the results were expressed as the mean value \pm standard deviation.

6.2.4 Analysis of moisture content

The moisture content of the potato strips was measured by drying the samples in a convection oven until constant mass at 65 °C. Analysis was conducted in triplicate for each individual experiment. The results were the mean of the triplicate experiments and expressed as $\text{g}\cdot\text{kg}^{-1}$.

6.2.5 Analysis of oil uptake

2 g of dried potato sample was put in a Soxhlet extractor for 4 h using petroleum ether. After extraction, the samples were dried for 30 min at 100 °C. The oil content was calculated by the difference between the initial weight and the end weight of each sample, and the results were expressed as $\text{g}\cdot\text{kg}^{-1}$ (AOAC, 2005; Method 934.01).

6.2.6 Analysis of asparagine

Asparagine was determined according to the assay (K-ASNAM) procedure of Megazyme International 2014. Briefly, 1 g of fresh potato sample was homogenized in 10 mL of water for 3 min. Following centrifugation (1000 rpm \times 10 min, 4 °C), the concentration of the clear supernatant was between 0.005 and 0.50 g/L. 0.1 mL sample solution, 0.02 mL glutaminase, and pH 4.9 buffer were mixed and incubated for 5 min at room temperature. Then, 1.6 mL distilled water, 0.3 mL buffer (pH 8.0) and 0.2 mL NADPH were added, and the solution was mixed and incubated for 5 min at room temperature. The reaction was started by the addition of 0.02 mL glutamate dehydrogenase suspension and the solution was mixed, and the absorbance of the solutions (A_1) was read by a spectrophotometer at 340 nm after 5 min and at 1 min intervals until the absorbance remained the same, indicating the

end of the reaction. Then, 0.02 mL asparaginase was added, and the absorbance of the solutions (A_2) was read after 5 min and at 1 min intervals until the absorbance is constant. The blank solutions include all the reagents of the samples without the 0.1 mL of sample solution. The asparagine was calculated as $[(A_1-A_2)_{\text{sample}} - (A_1-A_2)_{\text{blank}}] \times 0.4949$. If the sample has been diluted during the preparation, the result must be multiplied by the dilution factor. The results were expressed as $\text{g} \cdot \text{kg}^{-1}$ of fresh weight, and each sample was analysed in triplicate.

6.2.7 Analysis of sugars

Fresh samples (5 g) were extracted by refluxing for 30 min with 40 ml of 70% ethanol. The extract was vacuum-filtered, and the filtrate was diluted to 50 mL with ethanol. A 5 mL aliquot of the solution was passed through a Waters Sep-Pak C_{18} column and filtered (0.45 μm pore-size membrane), and then 20 μL of each filtrate was injected into a Hewlett Packard series 1100 high-performance liquid chromatograph (HPLC) equipped with a Beckman 110B injector and a Beckman Refraction Index Detector (RID). The separation was performed using a Phenomenex Lunacolumn (250 x 4.6 mm i.d.), following (with a few modifications) the procedure of Hernandez et al. (1998). The mobile phase consisted of acetonitrile/water (78:22, v/v), and the flow rate was $1.8 \text{ mL} \cdot \text{min}^{-1}$. Individual sugars (fructose, glucose and sucrose) were identified and quantified using external standards. Each sample was analysed in triplicate. The sugar contents were expressed as $\text{g} \cdot \text{kg}^{-1}$ of fresh weight.

6.2.8 Analysis of acrylamide

The determination of acrylamide was conducted following (with a few modifications) the procedure of the gas chromatograph (PerkinElmer). 1 g of lyophilized powder was combined with 10 mL 0.1% formic acid solution and mixed on a wrist action shaker for 20 min. The mixture was refrigerated for 40 min for easier removal of the top oil layer. A 3 mL

aliquot of the clarified aqueous phase (beneath the oil layer) was filtered through a 0.45 μm nylon syringe filter and stored for clean-up and analysis. The SPE tube was preconditioned with 2 mL acetone, followed by 2 mL 0.1% formic acid, at the rate of one drop per second, and the acetone and formic acid were discarded. 2 mL of the filtered extract solution was subjected to solid-phase extraction (SPE) (CarboPrepTM 200 tube, 6 mL, 500 mg) with only gravity flow. The SPE tube was washed with 1.0 mL water and the solution was quickly passed through the tube. Vacuum was used for up to 1 min to dry excess water from the tube. The acrylamide residue in the SPE tube was eluted with 2 mL of acetone with using gravity only and collected for GC-FID analysis.

The GC analysis of the extract samples was performed on an AutoSystem gas chromatograph equipped with a flame ionization detector (FID) (Hewlett Packard 5890 series II). The column used was an Agilent HP-FFAP capillary (length=25 m, i.d.=0.2 mm, and thickness=0.3 μm), and the analysis conditions were as follows: the initial column temperature was settled at 100 °C for 0.5 min, then raised at a gradient of 10°C/min to 200 °C; the temperatures of the injector and detector were set to 250 and 260 °C, respectively; helium was used as the carrier gas at a flow rate of 1 mL/min and a splitless of 1 min, and the injection volume was 1 μL . The results were expressed as $\mu\text{g}\cdot\text{kg}^{-1}$ of lyophilized weight (LW).

6.2.9 Statistics

The data reported was the mean of triplicate independent experiments. The variations were evaluated through one-way analysis of variance (ANOVA) using Minitab 16 Statistical software (MINITAB Inc, State College, PA, USA). Differences between mean values were evaluated using the HSD Tukey test with a 95% confidence interval. Pearson's correlation analysis was carried out to study the relationships between variables.

6.3 Results and discussion

6.3.1 Influence of frying temperature on acrylamide formation

It is well-known that commercial potato strip production prefers to use the cultivars with lower reducing sugar (glucose and fructose) and asparagine contents. Although an upper limit has not been specified for cultivars suitable for potato frying production, CIAA (2009) advised the use of potato cultivars with a reducing sugar content of less than 3 g.kg⁻¹ fresh weight for use in fried potato products. In this study, three cultivars were selected: one (Red Pontiac) with a reducing sugar content of more than 3 g.kg⁻¹ fresh weight and two (Agria and Kennebec) with contents of less than 3 g.kg⁻¹ fresh weight. The concentrations of the assumed precursors of acrylamide (glucose, fructose and asparagine) are shown in Table 6.1. The concentrations of glucose in the Red Pontiac and Kennebec cultivars were 3.14 and 1.26 g.kg⁻¹ fresh weight, while the fructose concentrations were 1.76 and 0.85 g.kg⁻¹ fresh weight, respectively. The contents of glucose and fructose in the Agria cultivar were the lowest of the three cultivars. The values of asparagine ranged from 2.03 to 3.21 g.kg⁻¹ fresh weight, which is in line with the values (0.15-4.58 g.kg⁻¹ fresh weight) reported for different cultivars by Vivanti et al. (2006).

Influence of the frying process and potato cultivar on acrylamide formation in French fries

Table 6.1 Properties of fresh potato samples

Cultivar	Color parameters				Texture parameters					Asparagine (g.kg ⁻¹ FW)	Sugars (g.kg ⁻¹ FW)		
	L*	b*	C	H(°)	Shear force (N)	Hardness (N)	Springiness (mm)	Cohesiveness	Chewiness (N.mm)		Fructose	Glucose	Sucrose
Kennebec	68.13±2.55a	12.71±0.48b	12.86±0.90b	98.79±0.14b	31.22±2.34a	227.20±3.90a	0.61±0.10a	0.11±0.02b	15.41±1.37a	2.03±0.08c	0.85±0.02b	1.26±0.02b	0.87±0.05b
Red Pontiac	67.88±2.26a	10.86±0.41b	11.02±0.82b	99.80±0.36a	30.15±1.09a	265.31±5.62a	0.53±0.08a	0.15±0.01a	21.00±2.42a	2.54±0.13b	1.76±0.03a	3.14±0.15a	1.48±0.04a
Agria	63.64±1.71a	27.49±1.11a	27.83±1.08a	98.99±0.86ab	35.40±2.16a	230.20±4.70a	0.54±0.10a	0.14±0.01ab	13.95±2.88a	3.21±0.04a	0.69±0.01b	0.69±0.01c	1.31±0.06a

Values are expressed as mean values ± standard deviations.

One-way balance ANOVA by Turkey's test was performed and the mean values with different small letters are significant in columns (P <0.05).

The frying time and oil temperature should be controlled to avoid high acrylamide levels, and the temperature should not exceed 170-175 °C (Vinci et al., 2012). Thus, in this study, 150, 170 and 190 °C were selected for assessing the effect of temperature on acrylamide formation. The acrylamide levels of potato strips prepared by frying at 150, 170 and 190 °C are shown in Figure 6.1; the contents for all tested cultivars ranged from 1975 to 5563 $\mu\text{g.kg}^{-1}$ LW for 150 °C, 3124 to 5814 $\mu\text{g.kg}^{-1}$ LW for 170 °C, and 4424 to 6035 $\mu\text{g.kg}^{-1}$ LW for 190 °C, which are values slightly higher than those previously reported for fried potato products in other studies (Pedreschi et al., 2004; Pedreschi et al., 2006) because of the different frying conditions and potato cultivars. The lowest acrylamide content was found in the Kennebec cultivar. The acrylamide levels changes varied with the temperature and cultivar. As Figure 6.1 shows, the acrylamide content steadily increased with the frying temperature from 150 to 190 °C for the Kennebec cultivar; it significantly increased as the frying temperature increased from 150 °C to 170 and 190 °C for the Red Pontiac cultivar; and it slightly increased with the temperature for the Agria cultivar. Hence, a higher temperature results in a higher acrylamide level in fried potato products, in agreement with other studies (Palazoglu et al., 2010; Pedreschi et al., 2006), but the degree of increase was not the same for different potato cultivars, which was attributed to the different contents of the acrylamide precursors and moisture.

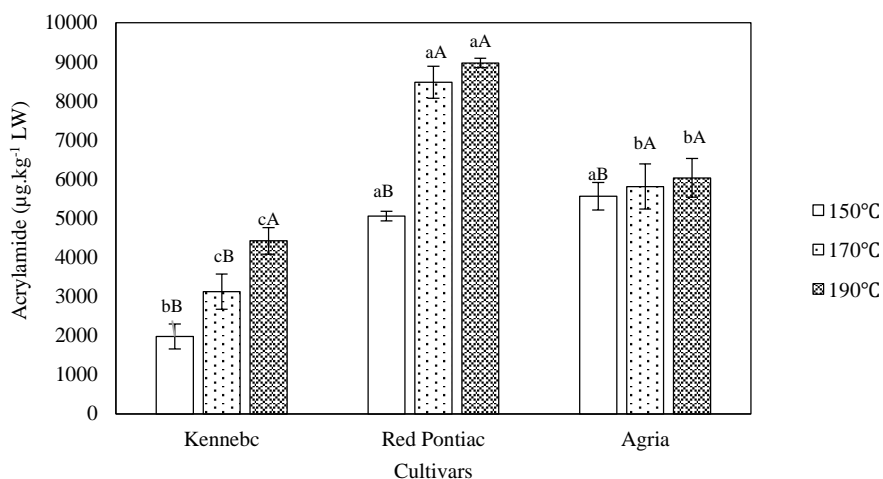


Figure 6.1 Acrylamide levels of fried potato cultivars prepared by different temperatures. a-c: Means with different small letters are significant ($p < 0.05$) in different cultivars at same temperature. A-C: Means with different capitals are significant ($p < 0.05$) in different temperatures at same cultivar.

Correlations between the acrylamide in the fried potatoes and the concentrations of asparagine and sugars were investigated for all the tested cultivars together and separately for the individual cultivars and revealed some unexpected differences. There was a significant correlation between the asparagine concentration and acrylamide level ($r=0.423$, $P<0.05$) (Table 6.2), but no significant correlations were found for the individual cultivars. As Figure 6.2 shows, the Kennebec cultivar, with the lowest acrylamide content, had a lower asparagine level; the asparagine content of Agria was the highest of the three cultivars tested, but its acrylamide level was not higher than the content of Red Pontiac, which is consistent with the report of Vinci et al. (2012), who reported that the asparagine concentration is generally in excess compared to the reducing sugar content in some cultivars, so that the reducing sugar content is the limiting factor in acrylamide formation.

Table 6.2 Correlations between acrylamide level and oil uptake and the factors potentially involved in the formation of acrylamide and oil uptake in all tested cultivars

	Acrylamide	Oil uptake
Asparagine	0.423*	-
Fructose	0.621**	-
Glucose	0.663**	-
Sucrose	0.699**	-
Reducing sugar	0.652**	-
Oil uptake	-0.505**	-
Moisture	-0.163	-0.224
L*	-0.586**	0.738**
b*	0.420*	-0.026
C	0.479*	-0.007
H	-0.284	0.569**
Shear force	0.749**	-0.375

Significant values are expressed: * $P<0.05$, ** $P<0.01$.

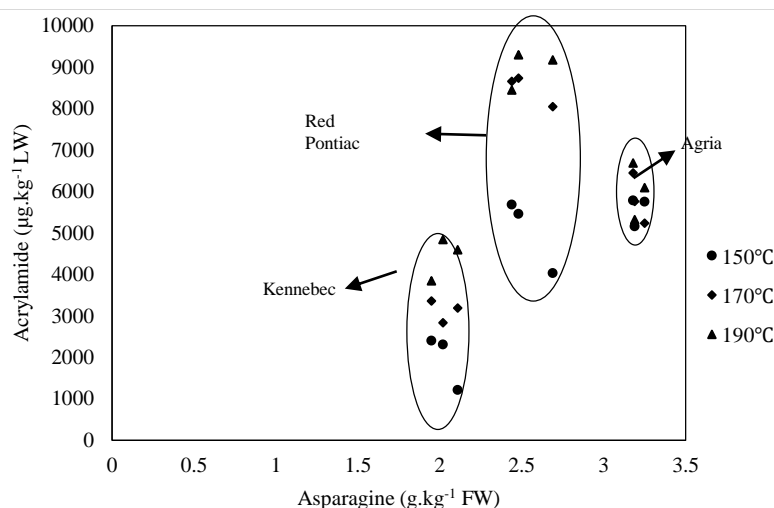


Figure 6.2 Acrylamide levels vs. asparagine for fried potato cultivars prepared by different temperatures.

The correlation between reducing sugar and acrylamide contents is also shown in Table 6.2. Overall, there was a significant correlation ($r=0.652$, $P<0.01$), but considering the individual cultivars, it was only found in Red Pontiac ($r=0.626$, $P<0.05$). The differences between the individual cultivars were more apparent when acrylamide was correlated with fructose and glucose concentrations. Overall there were significant correlations between fructose and acrylamide ($r=0.621$, $P<0.01$) and glucose and acrylamide ($r=0.663$, $P<0.01$), and a significant correlation within the three cultivars was only found in the Red Pontiac cultivar for fructose ($r=0.614$, $P<0.05$) and glucose ($r=0.615$, $P<0.05$). As Figure 6.3 shows, the Red Pontiac, with the highest acrylamide content, generally contained the highest reducing sugar content, while the reducing sugar content of Agria was the lowest of the three cultivars, but the acrylamide content was higher than that of Kennebec, which is not consistent with

several studies (Marquez & Anon, 1986; Amrein et al., 2003) that reported significant correlations between the reducing sugar and acrylamide contents. Therefore, the mechanistic pathway of acrylamide formation is complex, and it is not possible to say whether this is the explanation for these contrasting correlations without more detailed kinetic studies of the acrylamide formation. However, it may provide the new evidence to prove the suggestions of Halford et al. (2012), who reported that when the sugar content was relatively high, the acrylamide formation was proportional to the sugar concentration.

There was a significant correlation between sucrose content and acrylamide formation ($r=0.699$, $P<0.01$). However, sucrose was not considered a precursor of acrylamide formation because the sucrose concentration was significantly correlated with reducing sugars ($r=0.610$, $P<0.01$), so it may not necessarily reflect a direct relationship. Sucrose has been shown to contribute to acrylamide formation, which may be due to the hydrolysis through an enzymatic, thermal or acid-catalysed reaction (Halford et al., 2012).

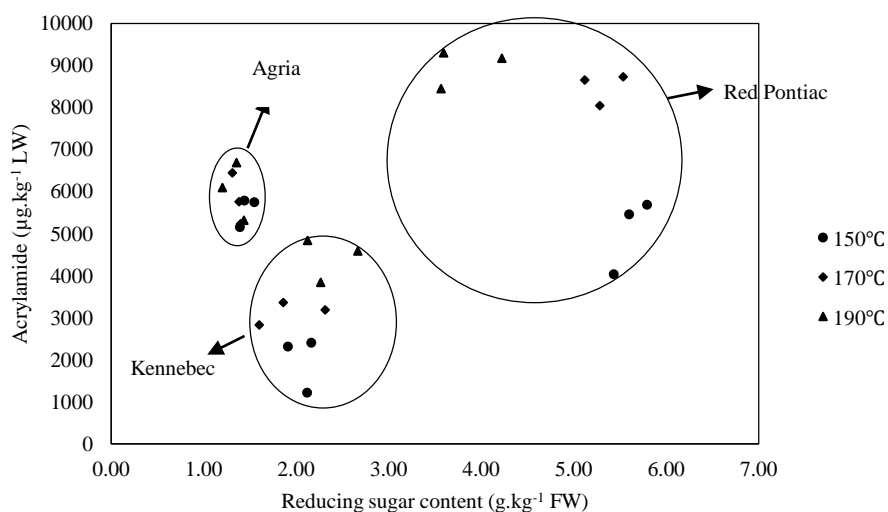


Figure 6.3 Acrylamide levels vs. reducing sugar content for fried potato cultivars prepared by different temperatures.

6.3.2 Relationship between acrylamide formation, oil uptake and moisture content

Oil uptake and acrylamide formation

The oil uptake is a complex mechanism that is not clearly understood, and the initial product structure, the interchanges between the product and the heating medium, and the variations in the product and oil properties are the factors that explain this phenomenon (Ziaiifar et al., 2008). The oil uptake in the three cultivars after frying at different temperatures is shown in Figure 6.4. The oil uptake decreased as the frying temperature increased from 150 to 190 °C for all tested cultivars, although this effect was more evident in previous studies (Moyano & Pedreschi, 2006; Pedreschi & Moyano, 2005). Increasing the temperature from 150 to 190 °C significantly reduced the oil uptake only for the Kennebec cultivar, as the extents of reduction for the Red Pontiac and Agria cultivars were not great. This trend was similar to that of the acrylamide levels at different temperatures. The correlation between the oil uptake and acrylamide formation was significantly negative ($r=-0.505$, $P<0.01$) in all analysed cultivars after frying. However, a much stronger and significant correlation was found in the Kennebec cultivar ($r=-0.781$, $P<0.01$); weak correlations were found in the Red Pontiac ($r=-0.427$, $P=0.252$) and Agria ($r=-0.379$, $P=0.315$) cultivars. Oil uptake reduction is also very important when frying potato strips. Therefore, the relationship between the oil uptake and the acrylamide formation necessitates that we find an optimum frying condition to obtain lower levels of both acrylamide content and oil uptake.

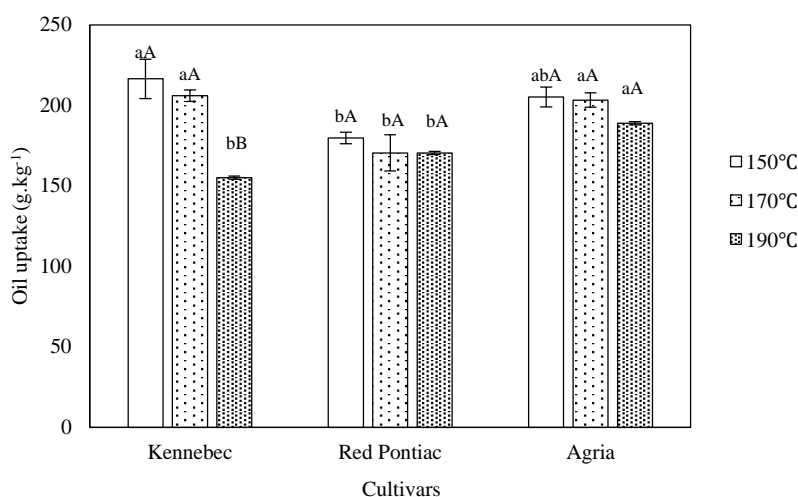


Figure 6.4 Oil uptake of fried potato cultivars prepared by different temperatures. a-c: Means with different small letters are significant ($P<0.05$) in different cultivars at same temperature. A-C: Means with different capitals are significant ($P<0.05$) in different temperatures at same cultivar.

Moisture content and acrylamide formation

The difference in the moisture content between the cultivars and temperatures was not great (Figure 6.5) because decreasing the temperature necessitates increasing the frying time, resulting in a similar final moisture content. However, the moisture content slightly increased with the temperature from 150 to 190 °C, ranging from 572 to 697 g.kg⁻¹, which was coincident with those reported by Predreschi & Moyano. (2005).

Amrein et al. (2006) reported a strong effect of the moisture content on the activation energy of acrylamide formation, which explains why lower temperatures for longer times are known to yield lower acrylamide levels in the final product. It was also reported that decreasing the moisture content tends to end of the frying process. The correlations between the moisture content and acrylamide level are shown in Table 6.2; the moisture content

presented weak negative correlations with the acrylamide level in all cultivars ($r=-0.163$, $P=0.417$), but strong correlations were found in the Kennebec ($r=0.928$, $P<0.01$) and Red Pontiac ($r=0.595$, $P<0.05$) cultivars.

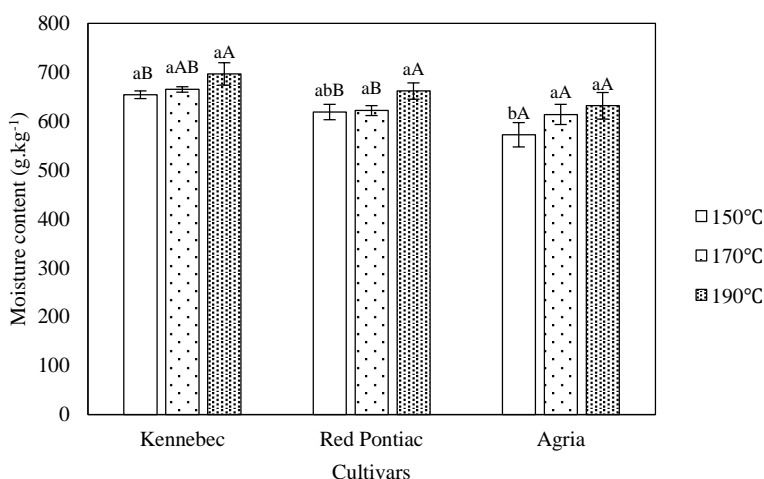


Figure 6.5 Moisture content for potato cultivars fried at 150, 170 and 170 °C. a-c: Means with different small letters are significant ($P<0.05$) in different cultivars at same temperature. A-C: Means with different capitals are significant ($P<0.05$) in different temperatures at same cultivar.

Moisture content and oil uptake

Gamble et al. (1987) found that moisture loss and oil uptake are interrelated, and both are linear functions of the square root of the frying time. In addition, Ziaifar et al. (2008) reported that the more water is removed from the surface, the more oil is absorbed. The moisture content in this study is the final content after frying, and the higher the final moisture content, the less was lost.

The correlations between the moisture content and oil uptake after frying at different temperatures were investigated for all tested cultivars (Table 6.2), and the correlation ($r=-0.224$, $P=0.261$) was negative but not significant. However, a significant negative

correlation was found in the Kennebec cultivar ($r=-0.778$, $P<0.05$), which is in agreement with the report by Southern et al. (2004). As a result, the oil uptake tends to decrease as the final moisture content increases during frying, which is in agreement with other studies (Gamble et al., 1987; Ziiaifar et al., 2008). However, the results also showed that there may be a characteristic curve of oil uptake against moisture content, and the curves for the different cultivars may be distinct.

6.3.3 Correlations of acrylamide formation and oil uptake with instrumental sensory parameters: colour and texture

Colour, acrylamide formation and oil uptake

The colour values are shown in Figure 6.6. The L^* and H values tended to decrease and the b^* and C values increased compared to their original values in the Red Pontiac and Kennebec cultivars, but the change of colour in the Agria cultivar between the fresh and fried potato strips was slight, which may be due to the reducing sugar content in the fresh potatoes. L^* tends to decrease as the frying temperature is increased from 150 to 190 °C, which means that the potato strips get darker. b^* refers to the yellowness, and b^* and C (positively correlated with the colour parameters of a^* and b^*) tend to increase, which proves that the frying strips get more red and yellow as the frying temperature increases; the H value decreased as the frying temperature increased.

Table 6.2 shows that the colour parameters presented significant correlations with the acrylamide content of the potato cultivars. The correlation in all cultivars between the L^* value and acrylamide content was significant and negative ($r=-0.586$, $P<0.01$), while the b^* and C values presented positive significant correlations with the acrylamide content for all tested cultivars ($r=0.420$ and 0.479 , $P<0.05$, respectively). However, the H values showed no significant correlations with the acrylamide content in all cultivars. Furthermore, the lightness of the frying strips decreased as the acrylamide formation increased, which was attributed to the potato strips getting darker as a result of Maillard reactions, while the

changing of the C and H values (C increased and H decreased) as the frying temperature increased is because of the Maillard non-enzymatic reaction development (Pedreschi et al., 2006).

The oil uptake vs. colour parameters in potato cultivars fried at 150, 170 and 190 °C are shown in Table 6.2. There is clear effect of the colour parameter values on the oil uptake in the cultivars: the L* and H values showed good correlations with the oil uptake ($r=0.738$ and 0.569 , $P<0.01$, respectively); the b* and C values showed negative and no significant correlations with the oil uptake in all cultivars. This shows that the colour of the frying strips gets darker as more oil is taken up.

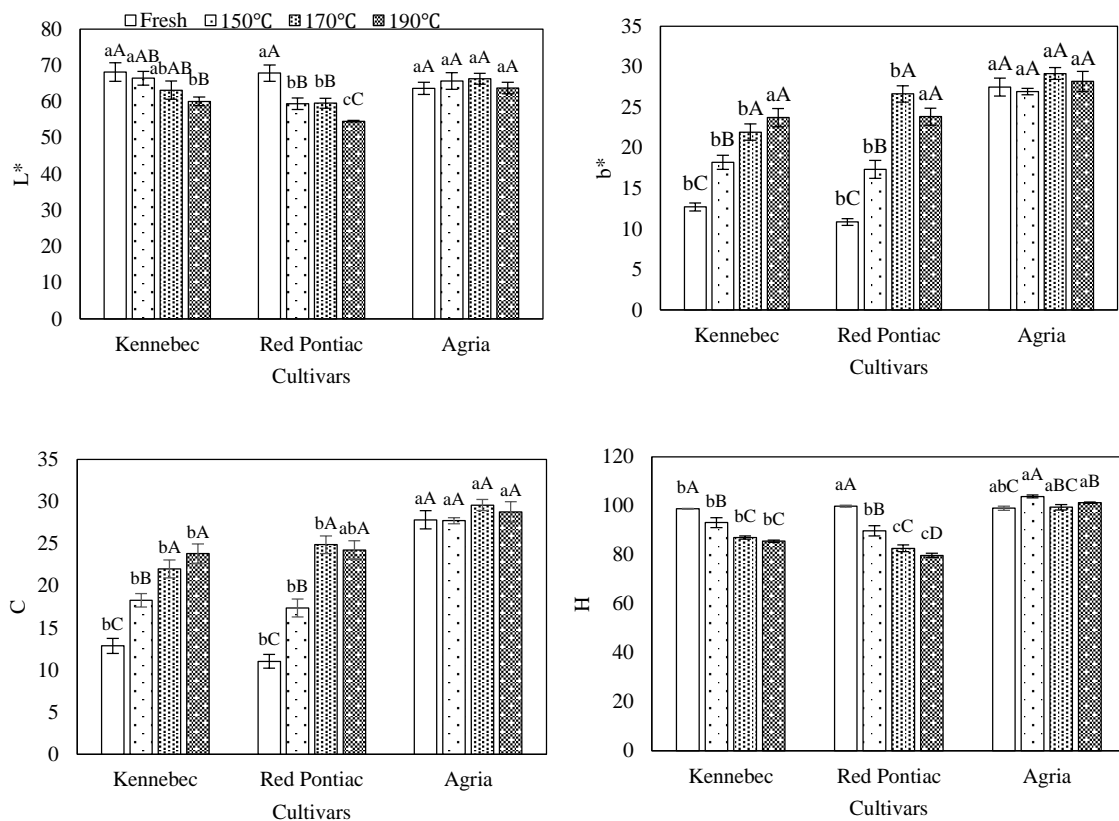


Figure 6.6 Development of the color parameters (L*, b*, C and H) of potato cultivars at different frying conditions. a-c: Means with different small letters are significant ($P < 0.05$) in different cultivars at same temperature. A-D: Means with different capitals are significant ($P < 0.05$) in different temperatures at same cultivar.

Texture parameters, acrylamide formation and oil uptake

The textural changes in the potato cultivars fried at 150, 170 and 190 °C are shown in Figure 6.7. Compared to the textural values of fresh potatoes (Table 6.1), the shear force, hardness and chewiness decreased significantly, and the changes in the springiness and cohesiveness were slight. The shear force and hardness decreased because of the starch gelatinization and lamella media solubilisation during frying (Andersson et al., 1994). The difference in the textural values between the different temperatures was not significant, which is attributed to the higher temperature necessitating a shorter frying time, affecting the final textural values. Only the shear force of the textural parameters presented a positive significant correlation with the acrylamide content ($r=0.749$, $P<0.01$) but a not significant and negative correlation ($r=-0.375$, $P=0.054$) with oil uptake in the cultivars (Table 6.2). The negative and significant correlation of L* with the shear force was found in all cultivars after frying ($r=-0.648$, $P<0.01$). In addition, there were negative significant correlations between L* and the shear force in the Red Pontiac and Kennebec cultivars ($r=-0.777$ and -0.439 , $P<0.05$, respectively).

Therefore, when frying at 190 °C, the potato strips were harder and darker and contained less oil and higher acrylamide levels than potato strips fried at 150 °C in all cultivars, which agreed with Pedreschi & Moyano. (2005).

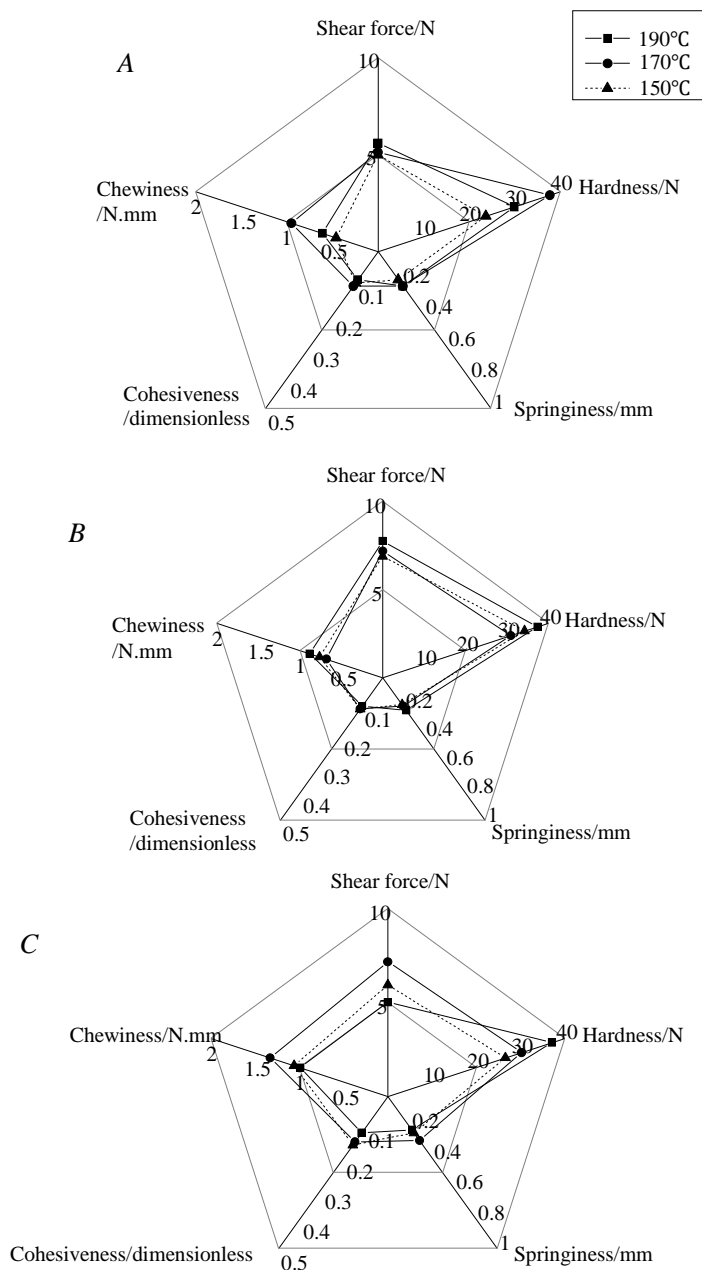


Figure 6.7 Textural analysis parameters for different potato cultivars (A/Kennebec; B/Red Pontiac; C/Agria) caused by different frying conditions.

6.4 Conclusions

The composition of the fresh potato cultivar is the primary factor in the formation of acrylamide. However, apart from the reducing sugars and asparagine, there are other factors affecting the acrylamide formation. In our present study, sucrose and oil uptake may play a role in the final concentration of acrylamide. For the Agria cultivar with a lower reducing sugar content, the possible hydrolysis of sucrose during the frying process may cause acrylamide production. Additionally, frying the potato strips at 190 °C resulted in more acrylamide, less oil uptake, more moisture, and darker and harder strips than those fried at 150 °C. The significant correlations of the lightness and shear force with the acrylamide content indicated that the darker and harder French fries contained higher acrylamide levels. A significant correlation between the oil uptake and acrylamide content was found in all tested cultivars, possibly indicating that the contribution of the oil uptake to the formation of acrylamide should not be neglected.

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Chapter 7

General results

In this chapter the principal results obtained in this thesis are presented. For each secondary objective we highlight the main contributions of the research work and we discuss their implications in the field.

1) To evaluate eight potato cultivars commonly consumed and study the relationship between their chemical and physical properties to determine their processing aptitude.

Eight common potato cultivars (Agata, Agria, Caesar, Cherie, Kennebec, Monalisa, Red Pontiac and Spirit) were characterized.

The **physical properties** are significant different between potato cultivars. The chroma and hue-angle values of the tubers varied considerably. The chroma values of the yellow and light-yellow tubers were higher than those of the white tubers. The highest Hue-angle value was obtained for Agata (light yellow) > Monalisa (light yellow) > Spirit (white) tubers \geq Agria (yellow), Caesar (light yellow), Cherie (yellow) Red Pontiac (light yellow). The differences in Shear force (She) and the textural properties: cohesiveness (Coh), chewiness (Che), hardness (Har) and springiness (Spr) among the potato cultivars may be due to their differing dry-matter content (DM).

Chemical parameters. Significant differences were found in the sugar content of the potatoes of the eight cultivars tested ($P < 0.05$). The concentration of glucose was slightly higher than that of fructose in all the cultivar samples. These parameters are very important in potato processing such that the higher the reducing sugar content, the higher the level of browning after frying since may be a potential risk for acrylamide formation during cooking.

The major component of the starch profile in raw potato is the resistant starch (RS), 65-85% of the total starch, type 2 (RS2, ungelatinised resistant granules that are slowly hydrolysed

by α -amylase). There were significant differences between the RS contents of the cultivars ($P<0.05$).

For the first time the presence of lactic acid was detected in some potato cultivars. The total phenolic content (TPC) of the potato skin and flesh were significantly different between cultivars. Negative correlations were found between the DM and TS contents and the TPC content. The antioxidant activity (AA) in the flesh and skin extracts of the potato cultivars were significant different ($P<0.05$). The yellow and light-yellow flesh of the cultivars exhibited significant higher AA compared with those of the white-flesh potato cultivars. The positive correlations are found between the ORAC values of the flesh and skins potato and their TPC ($r=0.984$; $P<0.01$ and $r=0.659$; $P<0.01$) respectively.

We stated that the textural attributes are important for describing the variation between common potato cultivars. Significant Pearson's correlations were found due to the common and complex interactions between the constituents of potatoes and their properties ($P<0.05$). Principal component analysis (PCA) revealed the correlations among the physicochemical properties, and the first two principal components explained 56.84% of the variance among the cultivars studied. Moreover PCA led to the classification of the potato cultivars: (1) Cherie, Kennebec, Agria, Caesar and Red Pontiac; (2) Agata and Monalisa; (3) Spirit. The group 1 and group 3 cultivars were recommended for frying owing to their higher hardness and DM content and lower reducing sugar content, while the group 2 cultivars were recommended for boiling and baking because of their higher values of springiness, cohesiveness and chewiness, and not peeling the cultivars increased their antioxidant properties. Certain nutritional and functional parameters of the different cultivar groups indicated the potential efficacy of different cultivars to satisfy the nutritional needs of consumers and industrial use. These properties and groups may explain and reinforce the cooking types of cultivars proposed by the European Cultivated Potato database.

2) To study the effect of temperature and time of boiling, baking and microwaving treatments on the nutritional components and physical properties of commercial potato tubers selected.

Four potato cultivars were selected (Agata, Caesar, Kennebec, Red Pontiac) according to the reported by Chapter 4 (Caesar, Kennebec and Red Pontiac belonged to group 1 and Agata belonged to group 2) and their cooking type defined by the European Cultivated Potato database. The effect of time-temperature was evaluated in three cooking methods: boiling, baking and microwaving on the physical and chemical properties of potatoes.

The **core temperature** curves obtained for the different cultivars in the same treatment were similar. Nevertheless, equal treatment but different cooking conditions were distinct, especially for microwaving. Additionally, this treatment was remarkable different from baking and boiling. In all cooking processes the initial gelatinization process of starch start at 60 °C, but between 82 °C and 90 °C, the potato starch completely gelatinized for a very short time.

Chemical properties. The cooking treatments entailed a new starch profile in all the cultivars. In general, the effect of heat-treatments implied a remarkable reduction of the resistant starch (RS) content and an increase in the soluble starch content. The highest RS content percentage of the original value of the raw samples in average of all cultivars was in baking potatoes. The individual sugars (fructose, glucose and sucrose) increased by baking and microwaving compared with raw tubers, with the highest increase shown by baking treatment in all cultivars, especially the baking at 250 °C for 60 min. The results obtained showed that the lower core temperature during boiling, the higher temperature and shorter time of baking and the lower power of microwaving were good for retain the total phenolic compounds TPC in the potato flesh of cultivars. Additionally, the higher losses of TPC in the potato skin are obtained in boiling and microwaving, on the other hand, TPC were

slightly increased by baking in all the cultivars. The average content of antioxidant activity (AA) in flesh samples was increased by all cooking methods. The cv. Agata had the most favorable influence on the AA of flesh samples (increased to 174% ~215% of original value).

Physical properties. Boiling obtained the minimum weigh losses for all the cultivars (< 2 %) whereas baking obtained the highest values (>20 %). For microwaving weigh losses were < 15 %. The possible differences on the microstructure of the potato peel may affect the water evaporation during the cooking procedures. The treatments affected in a similar way the dry matter content of potatoes independently of the initial value. The softness of cv. Agata was higher than the other cultivars; moreover boiling and baking were the treatments that had a higher impact on the hardness and shear force. Highly significant Pearson correlation coefficient was found between dry matter and hardness (0.700; $P<0.001$). The boiling treatments showed lower chewiness values in all potato cultivars. The intensity of the treatment was not proportional to the color losses. Depending on the original color of the potato, losses were different between cooking treatments. After being cooked, lightness decreased significantly except for Caesar ($p<0.05$), which means that the potato samples get darker.

The principal component analysis (PCA) was a good way to prove the effect of the different treatments and cultivars on the properties of potatoes. The first two principle components accounted for 77.32% of the total variation (50.83% and 26.49%, respectively). PCA results primarily discriminated the cooked potato cultivars: the Agata cultivars from the Kennebec, Red Pontiac and Caesar cultivars, which also proved the classification groups of Chapter 4. After the heat treatments, the Agata cultivar exhibited higher AA, TPC, RS and C, and the other cultivars (Kennebec, Red Pontiac and Caesar) were associated with the higher TS, DM,

cooking degree, which were the textural parameter values and the color parameter (L and H) values.

The physical instrument properties may be considered the indicator of some nutritional and functional properties of cooking potato products, and certain nutritional and functional parameters of different cultivars after treatments indicated the potential efficacy to satisfy the nutritional needs of consumers and industrial use.

3) To assess the frying temperature and time on acrylamide content and to study the relationship between acrylamide levels and the factors potentially involved in its formation Three potato cultivars (Agria, Kennebec and Red Pontiac)

commonly used for fried products in Europe were analyzed to evaluate the influence of frying conditions (190 °C for 160 s, 170 °C for 240 s and 150 °C for 330 s) on acrylamide formation.

The acrylamide levels of potato strips increased with the frying temperature. The increase of acrylamide was different for each potato cultivar and frying temperature: for cv. Agria, acrylamide content was not affected practically by frying temperature whereas, cv. Kennebec was highly dependent on the frying temperature in the acrylamide formation. For cv. Red Pontiac the acrylamide formation was significantly different from 150 °C to 170 and 190 °C.

Chemical precursors of acrylamide. The individual sugars, fructose and glucose, were correlated with the acrylamide levels ($r=0.621$, $P<0.01$) and ($r=0.663$, $P<0.01$), respectively. In addition, a new significant correlation between sucrose and acrylamide content was obtained ($r=0.699$, $P<0.01$). This correlation can be attributed to the hydrolysis of sucrose through an enzymatic, thermal or acid-catalysed reaction. However, the correlation between asparagine and acrylamide content was lower ($r=0.423$, $P<0.05$).

Physical properties and acrylamide relationships. The differences in the textural values of French fries between the frying temperatures were not significant, that is attributed that the higher temperature and the shorter the frying time. However, shear force presented a positive significant correlation with the acrylamide content ($r=0.749$, $P<0.01$). The Maillard reactions during frying entailed the decrease of lightness (L^*) of the potato strips and the acrylamide formation increased. The L^* and H values showed good correlations with the oil uptake ($r=0.738$ and 0.569 , $P<0.01$, respectively). In consequence, the colour of the frying strips gets darker as more oil is taken up. The correlation between L^* value and acrylamide content was significant and negative ($r=-0.586$, $P<0.01$), while the b^* and chroma values presented positive significant correlations with the acrylamide content for all tested cultivars ($r=0.420$ and 0.479 , $P<0.05$, respectively).

The results indicate that frying at 190 °C, the potato strips were harder and darker and contained less oil and higher acrylamide levels than potato strips fried at 150 °C in all cultivars.

Chapter 8

Conclusions

CONCLUSIONS

The main objective of this research work was to study the effect of cooking processes: boiling, baking, microwaving and frying on the physical and chemical properties of potato cultivars consumed worldwide. For our experimental results some conclusions are presented following the specific objectives:

Objective 1: **Evaluation of the chemical and physical properties of potato cultivars to determine their processing aptitude.**

- The physical and chemical properties of the cultivars were notable different, which determined the aptitude of the potato cultivars on being processing. The group were suitable for frying which was due to the higher hardness, dry matter and the lower reducing sugar content, and the cultivars were fit for boiling and baking because of the higher value of springiness, cohesiveness and chewiness.
- We recommended for boiling and baking process don't remove the skin because increase the antioxidant properties.
- These results reinforce the cooking type of the cultivars proposed by the European Cultivated Potato database.

Objective 2: **The effect of temperature and time of cooking processing on the nutritional components and physical properties of commercial potato tubers.**

- Baking and microwaving processes involved higher weight losses for the evaporation of potato water across the skin, independently of the cultivar. All the cooking treatments affected similarly the dry matter content of potato independently

of the assessed cultivar; however microwaving process had higher values of dry matter.

- The intensity of the treatment is not proportional to the color losses after being cooked. The diffusion of water across the potato tissues may be responsible of the differences in softening but the softening after being cooked depended on the potato cultivar. Specific textural properties Shear force and Hardness are highly affected for boiling and baking. However, in any potato cultivar Chewiness and Springiness were remarkable different between cooking process.
- The core temperature affected the starch gelatinization of potato during process. The total and resistant starch decreased after processing and the resistant starch retention of baking and microwaving was higher than that of boiling. The individual sugars (fructose, glucose and sucrose) increased by baking and microwaving. The effect of the cooking process on the total phenolic compounds and antioxidant activity in potato flesh depends on the potato cultivar. However, the maximum retention of bioactive compounds was obtained with the lower core temperature during boiling, the higher temperature and shorter time of baking and the lower power of microwaving.
- The physical instrumental properties may be considered the indicator of some nutritional and functional properties of cooking potato products.

Objective 3: **Effect of the frying temperature and time on acrylamide content: the relationship between acrylamide levels and the factors potentially involved in its formation.**

- The composition of the fresh potato cultivar is the primary factor in the formation of acrylamide. However, apart from the reducing sugars and asparagine content, there

are other factors affecting the acrylamide formation: sucrose content and oil uptake may play a role in the final concentration of acrylamide.

- For the Agria cultivar, with a lower reducing sugar content, the possible hydrolysis of sucrose during the frying process may cause acrylamide production.
- Lightness and shear force are correlated with the acrylamide content indicated that the darker and harder French fries contained higher acrylamide levels. A significant correlation between the oil uptake and acrylamide content was found in all tested cultivars, possibly indicating that the contribution of the oil uptake to the formation of acrylamide should not be neglected.

In summary, the determination of potato physical properties has enabled a quick and effective evaluation of the effect of the culinary processes on potato cultivars. In addition, physical properties of potato can be used for predicting the acrylamide formation in French fries. The control of core temperature during processing is essential for maintain the nutritional and instrumental sensorial quality of cooked potatoes.