Process innovation and quality aspects of French fries

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Beatus, qui prodest, quibus potest.

Abstract

The development and evaluation of a new production process for French fries is described. Superheated steam was used to replace pre-drying in hot air and par-frying in oil, and vacuum cooling was used for cooling and freezing. Finish-frying was still carried out in oil. In this way a substantial reduction of energy use and environmental costs was possible. However, problems with product quality were encountered. The main problem was skin formation, which resulted in a tough crust with a fatty appearance after finish-frying. The new process was modified, and this improved the product quality considerably. Unfortunately, the resulting energy reduction was too limited to justify the investment required for the new process.

Furthermore, a new look into the quality aspects of French fries is presented using state-of-the-art equipment. A combination of sensory analysis, Texture Analyser, and Confocal Scanning Laser Microscopy was used to study crispness of French fries independent of moisture content and doneness. In this way a higher frying temperature was shown to increase crispness. Prolonged pre-drying in hot air caused blister formation, which was similar to the skin observed with superheated steam. Odour active compounds of French fries were identified using GC-MS and GC-Olfactometry. Subsequently, the release of some of these compounds was followed in real time with MS-Nose using assessors and a mouth model system. It was shown that increasing the frying time, adding salt, and also skin formation affect flavour release. Most of the identified flavour compounds originated either from the Maillard reaction or from lipid degradation. Acrylamide is formed in the Maillard reaction as well. Multiresponse modelling of acrylamide formation in a glucose-asparagine reaction system showed that acrylamide is an intermediate rather than an end product. Early lipid oxidation was studied at frying conditions by following the decrease of the antiradical power. Frying French fries was found to slow down the decrease of antiradical power, suggesting that compounds with antioxidative properties migrate from the product to the oil.

In conclusion, the work described in this thesis has contributed to insights into physicochemical processes that occur in French fries on micro-scale, and how process conditions influence the product quality.

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Chapter 1

General introduction

1.1 HISTORY OF FRENCH FRIES

The potato originates from the western part of South-America and was already cultivated 200 AD.[1] At the end of the 16th century it was introduced in Europe via two different routes. The Spanish brought an elongated, red-peeled potato variety from Peru to Middle-Europe. In the other route a yellow-peeled, flat-round potato variety was transported from Chile via Cartagena to England.[2] Until the middle of the 17th century the potato plant was used as ornamental plant only. It was thought that potatoes caused diseases such as leprosy, and some even considered potatoes as a dangerous aphrodisiac.[3]

How the potato finally became a popular staple food is not completely clear. Most likely the potato was grown as an emergency measure due to starvation. Nor is it clear who was the inventor of French fries. Frying foods had its origin in China around 3000 BC,[4] but potatoes were not cultivated there at that time. Whatever the case, by the 1830s deep-fried potatoes had become a popular taste sensation in both France and Belgium. In the 1880s the concept was transported to America. The first reference of French fries in literature was in 1894 in O. Henry's novel "Rolling stones".[5] The name French fries may originate from the people that introduced it in the USA or it was adopted by American soldiers during the WW I (although they were actually stationed in the French-speaking part of Belgium). Others believe that the name comes from the verb "to french" meaning "to cut into thin strings". A third explanation is that it is a misunderstanding of the archaic British usage of "French fried potatoes", referring to the way of preparation with two frying steps and cooling in between.[6]

About 60 years ago, after World War II, freezing techniques were developed that facilitated storage and distribution.[7] This was the time that the big fast food restaurants started their business, and a massive growth of the industrial production of French fries and other frozen potato products occurred. Today, the world production of fried, frozen potato products exceeds 4,500 million kg, of which French fries represent about 86%.[4] After the USA, the Netherlands is the largest potato processing country in the world with a production of more than 1,500 million kg of potato products in 2001.[8]

1.2 FRENCH FRIES PRODUCTION PROCESS

A general scheme for the production process of French fries is shown in Figure 1.1.

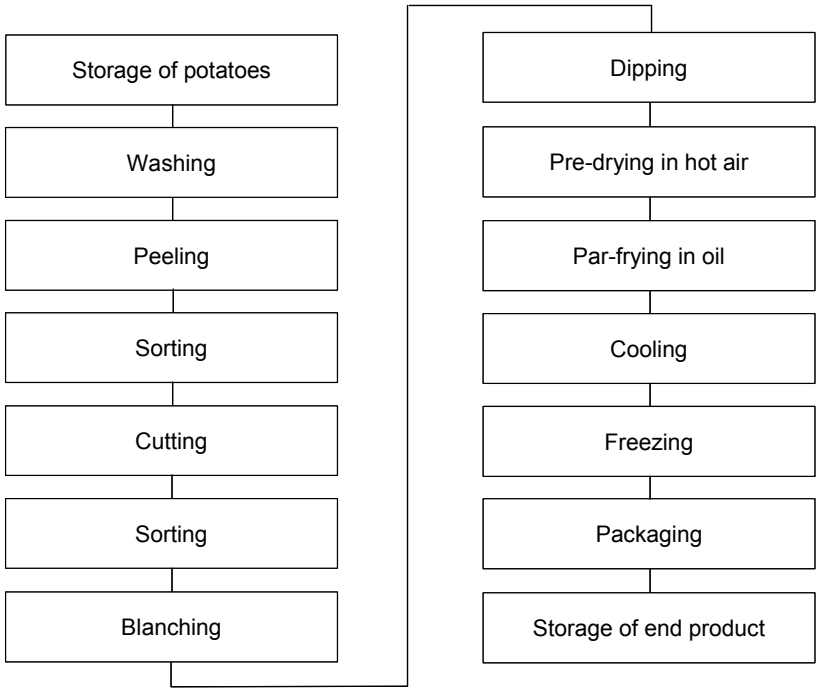

Figure 1.1 Scheme of French fries production process.

Storage conditions after harvesting are very important for further processing. High temperature storage induces sprouting, while cold storage increases the reducing sugar content.[9,10] Therefore, potatoes are usually stored at 6–8 °C and then reconditioned for 2 to 3 weeks at 15–18 °C before transportation.[11] After arrival at the factory a sample of potatoes is taken from every batch to determine the amount of reducing sugars and the dry matter content. Reducing sugars are responsible for colour formation in the Maillard reaction, and excessive amounts will result in a too dark product.[12,13] The dry matter content determines how much water has to be evaporated during further processing to reach the desired final moisture content. If the dry matter content of

the potato is too high, the crust will be hard and the inside dry. Low dry matter content will result in a weak crust and a wet inside texture.[7] The dry matter content and the amount of reducing sugars differ from year to year and within the season,[14] but also within batches and within a tuber.[15,16] Therefore, the process requires permanent adjustment according to the raw material characteristics in order to obtain a constant end product.[9] The chemical composition of potato tubers is shown in Table 1.1.

Table 1.1 Chemical composition of potato tubers.[17]

Substances	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 sugars	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	0.69–4.63	2.00
Lipids	0.02–0.2	0.12
Ash	0.44–1.87	1.1
Organic acids	0.4–1.0	0.6

Before peeling, potatoes are washed to remove soil, stones, and other foreign materials. Steam peeling is generally used because of low peel loss.[18] The high-pressure steam treatment (typically 16 bar) causes the water under the skin of the potatoes to boil very quickly, and the skin will separate from the flesh.[19] A water gun is usually applied to cut potatoes into strips. Potatoes are pumped in water at high velocity through a series of knife blades set to the required cutting size. Potatoes are oriented in such a way that they are cut longitudinally, obtaining maximum length and minimum waste.[19] Defects are detected with a camera and blown off with an air jet. The defect part is cut off and the strips re-enter the process. Potato strips are subsequently blanched in hot water. The main reasons for blanching are the inactivation of enzymes (polyphenol oxidase and peroxidase) and the control of reducing sugars in order to obtain a bright, uniform colour after frying.[20] Other functions of blanching are starch

gelatinisation, this reduces oil uptake during frying,[21] and texture improvement. Enzyme inactivation occurs quickly at elevated temperature (80–100 °C). Leaching of reducing sugars, on the other hand, takes time and a lower temperature (50–70 °C) is necessary to prevent overcooking. Therefore, blanching is often carried out in two steps.[20] The minimum blanching temperature applied in practice is about 65 °C, otherwise spoilage due to bacterial growth may occur. After blanching the strips are dipped in a solution of sodium pyrophosphate. Sodium pyrophosphate chelates metal ions that would cause discolouration.[7] Pre-drying in hot air prior to the frying step improves texture and reduces oil uptake. By removing surface water the beginning of a crust is made. Oil absorption is reduced, because the proportion of open pores is decreased during pre-drying due to shrinkage.[22] Also, a part of the moisture loss is realised, so that the par-frying time can be shorter.[7] Frying is traditionally carried out in two steps, par-frying and finish-frying, with a cooling step in between. Finish-frying has to be done close the place of consumption (cafeteria, fast-food restaurant or at home), as the product is consumed quickly thereafter. The time between par-frying and finish-frying is extended by freezing in order to make storage and distribution possible. During par-frying the product is processed in such a way that a short finish-frying step is enough to obtain French fries with the desired quality characteristics. During frying water is evaporated, the product is cooked, and a crust is formed. Also, about 5% of oil is absorbed depending on the cutting size. The Maillard reaction is intensified because of the high temperature and reduced moisture content at the surface, resulting in accelerated colour and aroma formation. After par-frying, oil adhering to the surface, is removed by a vibrating belt to minimise oil uptake. The product is subsequently cooled and frozen with cold air in a number of steps. It is important that freezing takes place quickly otherwise cell damage may occur, which has a negative influence on the product quality.[19,23]

Other types of French fries have a slightly different process. French fries, which are finished in the oven, are par-fried longer than frozen French fries, and sugar is added to the dipping solution to accelerate colour formation.[7] Cool-stored French fries, generally used by restaurants and cafeterias, are also par-fried longer than frozen French fries, and usually no pre-drying step is performed. Storage takes place under modified atmosphere at 0–4 °C reaching a shelf life of about 2 weeks.

1.3 QUALITY ASPECTS OF FRENCH FRIES

Research papers referring to the quality of French fries generally discuss appearance, colour, flavour, texture, and oil uptake.[14,24-26] Also, the oil used for frying is important for the quality [27,28] and, recently, the formation and amount of acrylamide have become a quality issue.[29] These quality aspects will be discussed in this paragraph.

Appearance

Appearance is inspected before, during and after the process and defects are undesirable. Defects can occur in the raw material or can be caused by processing. Examples of defects in raw material are diseases (e.g. rot, scab, and scurf), green discoloration due to solanine formation, and blue discoloration because of bruising. These defects are usually noticed during visible inspection after washing or cutting. During steam peeling the outer surface, directly under the skin, is overcooked and a so-called heat ring is visible.[18] This causes a bubbly surface after par-frying. Other examples of defects that may occur during processing are shattering and feathering due to inadequate cutting, and blistering because of excessive pre-drying.[30] Long, uniform strips are desired and only a small percentage of slivers, nubbins and broken pieces is allowed in the end product depending on the specifications.[31] Moreover, slivers may result in burnt pieces after par-frying.

Colour and flavour

Reducing sugars react upon heating with proteins and free amino acids in the Maillard reaction.[32] The Maillard reaction is a complex reaction, in which colour and flavour are formed.[33] Melanoidines, brown nitrogenous compounds of high molecular weight, are the end products of the Maillard reaction that are responsible for the typical golden-brown colour. Excessive amounts, however, result in a dark product with a bitter taste. Amino acids are present in potatoes in higher amounts than reducing sugars.[34] Therefore, the intensity of the Maillard reaction can be controlled by the amount of reducing sugars.[13] As already mentioned, in practice this is done by adjusting storage and blanching conditions. Flavour compounds can be formed through several pathways in the Maillard reaction, such as Strecker degradation.[35] However, many other factors influence flavour besides the Maillard reaction. Several flavour compounds

originate from the frying oil by lipid degradation.[36] The raw material and processing can affect flavour in a negative way. Examples are off-flavours, which may be obtained from the soil, and prolonged dipping in pyrophosphate will result in a sour taste. In a broader perspective, one could argue that the sauce and the amount of salt added to the product determine flavour perception during consumption to a large extent.

Acrylamide

Recently, high amounts of acrylamide (up to 1220 μg/kg) were found in fried potato products such as French fries.[37] This was alarming, as acrylamide is probably carcinogenic to humans.[38] It turned out that acrylamide was formed in the Maillard reaction from asparagine,[39,40] and asparagine is the most abundant amino acid present in potato.[34] Research has shown that control of the raw material and the process makes it possible to reduce the amount of acrylamide to an acceptable level of less than 100 μg/kg.[41] In paragraph 1.4 this will be discussed in more detail.

Texture

Texture is considered as one of the most important quality aspects of French fries. There is a clear difference between the interior and exterior: the interior has to be soft and mealy, whereas the exterior consists of a crispy crust.[42] The crust is formed during frying and generally has a thickness of about 1 mm.[43] About 80% of the crust's volume is made up of void space.[44] The interior consists of cooked and slightly dehydrated cells with a texture similar to that of cooked potato.[45] Upon heating potato tissue softens due to degradation of cell wall polysaccharides. Starch gelatinisation occurs quickly at around 68 °C, but this is less important for the texture.[46] As the cell wall is much thicker than the middle lamella between cells, separation of cells occurs rather than cell rupture.[47] This is schematically shown in Figure 1.2.

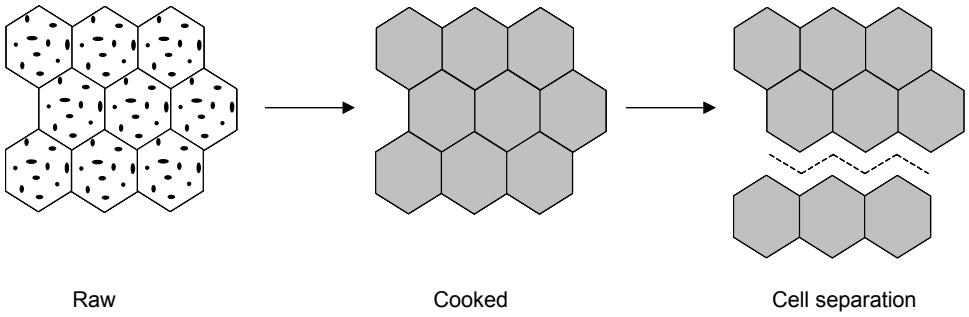

Figure 1.2 Scheme showing the effect of heat treatment on potato tissue.[17]

The cell structure remains intact in the crust as well. Cells are shrunken, wrinkled, and convoluted around the dried-gelled starch.[48,49] Cell separation occurs because of the build-up of pressure by evaporating water during frying. The mealy mouthfeel of cooked potato is caused by the shear of intact potato cells. The amount of filling in French fries is important for the mouthfeel. Low dry matter content or overcooking (either during blanching or during par-frying) will result in holes in the interior, which is undesirable. The mouthfeel of French fries also depends on the cutting size. With shoestring size French fries (7 × 7 mm) mainly the crust will be perceived, while the interior is more important for the traditional Flemish fries (15 × 15 mm).

Oil quality and oil uptake

Oxygen, light, high temperature, and water from the product cause degradation of the frying oil.[50] Degradation reactions can be divided in oxidation, hydrolysis, and polymerisation.[51] The visible changes that take place during frying include darkening, increased viscosity, decreased smoke point, and increased foaming.[52] Furthermore, volatile compounds are formed because of oxidation, which cause rancidity. This is important, because the oil affects the quality of the food being produced.[53] Fresh oil, however, does not obtain optimal frying results: products are not fully cooked and lack colour and flavour. Optimum frying conditions are only obtained after a certain heating time. This is explained by the formation of surfactants due to hydrolysis and oxidation.[54] Surfactants (e.g. mono- and diglycerides, polymers, phospholipids) increase the heat transition between the oil and the fried product by lowering the surface pressure. After

prolonged frying in the same oil the heat transition will be too high, and this results in dark, limp, and oily products. Industrial manufacturers like to keep par-frying oil in the optimum range as long as possible. This is done by continuous replenishment with fresh oil. Adding the same amount of oil to the fryer that is absorbed by the French fries keeps the oil quality constant.[28] Oil replenishment is not possible in the case of finish-frying due to the higher temperature, longer frying time, and lower product to oil ratio.

The type of oil that is used for frying is usually a compromise between stability and health aspects. Saturated fatty acids are very stable against deterioration at frying temperature, but are known to cause coronary heart diseases. Unsaturated fatty acids are beneficial for health, but especially polyunsaturated fatty acids are not very stable.[55,56] By hydrogenation the level of saturation can be increased, and this results in more stable oils. However, during hydrogenation also trans fatty acids are formed, and clinical studies have shown that these compounds are even more harmful than saturated fatty acids in causing coronary heart disease.[57,58] Therefore, vegetable oils with a lower degree of polyunsaturated fatty acids or blends of oils with different characteristics are used for frying.

Oil uptake strongly contributes to the caloric value of the product. Three mechanisms contribute to the oil content of a finished fried potato strip: oil that adheres to the surface after the product cools down; oil that enters into the crust by suction through pores after removal from the fryer; and oil that may be occluded in the forming crust during frying.[59] The latter is, however, a minor part, because most of the oil is taken up after removal from the fryer.[59-62] Oil is, therefore, almost exclusively present in the crust region.[30,43,49,63] Factors affecting oil uptake include frying time and temperature, surface to volume ratio, oil quality, porosity, moisture content, and pre-treatment (e.g. blanching and pre-drying).[64]

1.4 RESEARCH ON FRENCH FRIES

The frying process

Much of the research on French fries focussed on elucidating what happens in the product during frying.[7,9,45,65,66] Frying is generally recognised as a process of simultaneous heat and mass

transfer: heat is transferred from the oil to the product, water evaporates from the product, and oil is taken up.[24] After immersion into the oil the product surface reaches the boiling point quickly. Vaporisation of mainly free and capillary water takes place at a constant drying rate. Shrinkage mainly occurs in this part of the frying process.[7] Convective heat transfer in oil is 200-300 W/m^2K, and steam bubbles escaping from the material surface increase it up to 1200 W/m^2K by local micro-stirring.[66] The surface dries out fast and the vaporisation region is moving inwards. The surface region, from which water has evaporated, forms the crust. Although the surface temperature gradually increases, the temperature at the vaporisation region remains constant at 103 °C.[9] The high vaporisation rate creates a pressure gradient that drives liquid water towards the exchange surface, where it can be more easily vaporised. The crust becomes thicker as frying proceeds. The low thermal conductivity of the crust increases the resistance to the release of water vapour, and the vaporisation rate steadily declines. The pressure build-up below the crust results in the bursting of a few localised sites causing an increase in crust porosity.[45] Microscopic methods increased the insight in crust formation of fried potato to a large extent. It was shown that oil in the crust was like an "egg-box" surrounding intact dehydrated potato cells, but the oil did not penetrate into the cells.[49,63]

Optimisation of process steps

Several researchers have tried to model individual process steps in order to predict heat and mass transfer, and to further optimise the process. Especially the blanching and frying process received a lot of attention. The thermal properties of potato were studied and a simulation model for heat transfer during potato blanching was presented.[67] Further analysis showed that the thermal conductivity differs considerably between 50 and 100 °C.[68] Modelling of heat transfer was used to predict starch gelatinisation,[21,69] enzyme inactivation,[70] and textural changes [17] in potato tissue during blanching. Starch gelatinisation was found to take place quickly at 67.5 °C,[69] whereas a more intense heat treatment is required to soften the tissue. Mass transfer was studied in order to predict leaching of reducing sugars and ascorbic acid. At 60 °C an apparent diffusion coefficient of $11.3 \cdot 10^{-10}$ m^2/s was found for reducing sugars,[12] and $11.7 \cdot 10^{-10}$ m^2/s was found for ascorbic acid.[71] This means that during blanching not only reducing sugars are leached out, but considerable amounts of ascorbic acid are lost as well.[72]

Relatively simple empirical models have been developed to predict oil uptake during frying from the moisture loss.[22,30,73,74] This is because oil enters the voids from which water has evaporated.[62] Therefore, increasing the dry matter content prior to frying by for example pre-drying or osmotic pre-treatment results in a decreased uptake of oil.[22,74] Furthermore, oil uptake was found to increase with increasing frying temperature and decreasing sample thickness.[16,73,75,76] Modelling of heat and mass transfer in a fundamental way is, however, much more complex due to the changes in structure and physical properties that occur during frying. Farkas *et al*.[65,77] used two regions, the crust and the core, with a moving boundary to model frying of potato slices. However, they did not include the oil phase and the effect of the changing porosity on the heat and mass transfer.[78] Therefore, more work in this field is necessary to obtain a more detailed model for the frying process.

A universal method to improve raw material yield called production yield analysis was introduced by Somsen *et al*.[79] It can be used to monitor the efficiency of each process step by determining how much unwanted mass loss occurs during a step. Production yield analysis was applied to the production process of French fries, and a model to predict the maximum production yield was presented.[11,18,31] Raw material characteristics (amount of tubers per kg, under water weight, skin appearance, defect load, average cell size, reducing sugar content), additions (fat content), and product specifications (cutting size, target defect load, target reducing sugar content, target moisture content) influence the maximum production yield. Potential for improvement was found for the peeling process.

Quality improvement

Low-temperature blanching, typically at 50–70 °C, results in an increased firmness after cooking or frying.[20,80,81] In this temperature range the enzyme pectin methylesterase is active, which specifically hydrolyses methyl ester bonds of pectin increasing the number of carboxylate groups available to react with divalent ions such as Ca^{2+} and Mg^{2+}.[82] These interactions reinforce the cell wall structure, and enhance the resistance against thermal degradation.[83,84] Enzyme inactivation occurs in the same temperature range and, therefore, the residual activity strongly depends on the temperature distribution in the tissue.[70]

Several patents and articles appeared about the application of coatings to improve product quality.[85-92] Hydrocolloids such as starch, protein, gums or pectin were used as a coating and in most cases salts, surfactants, oil or stabilisers were added. Prior to pre-drying or par-frying potato strips were either dipped in the coating solution or the coating was sprayed on the strips. The coatings were used to reduce oil uptake, to enhance crispness or to retain crispness for a longer time after finish-frying.

It was about one year after the start of this thesis that acrylamide was recognised as a harmful compound present in fried potato products and some other foods in relatively high quantities.[29] Since then, literally hundreds of articles have been published focussing on analysis of foodstuffs for acrylamide, optimisation of analysis methods, disclosure of pathways of formation, factors affecting the formation, estimation of the health risk, and ways to reduce the amount of acrylamide formed. Recently, an extensive review about this subject appeared.[93] With regard to French fries, it was shown that the amount of acrylamide formed depends mainly on the amount of reducing sugars present,[94-96] as is true for other compounds formed in the Maillard reaction. From this perspective, ways to reduce acrylamide formation are obvious: selection of potatoes with low reducing sugar content, good storage conditions, adequate blanching, and a maximum frying temperature of about 170 °C.[41] Other measures proposed to reduce acrylamide formation were lowering the pH by dipping potato strips in a citric acid solution prior to frying,[97,98] degrading asparagine by a treatment with asparaginase prior to frying,[99] and lowering the frying temperature by vacuum frying.[100]

1.5 AIM AND OUTLINE OF THE THESIS

From the previous paragraphs it has become clear that many factors influence the final product quality attributes, and that there are many interactions among different quality aspects. Much effort has been undertaken to improve product quality, to optimise process steps and to make the process more efficient. However, the current process still has a number of major disadvantages. The energy use in the form of natural gas and electricity is high. Especially pre-drying in hot air, par-frying in oil, and freezing require a lot of energy. In the current process a part of the energy is recovered by using the heat from evaporated water in the frying oven to heat up pre-drying air.

Another disadvantage is the oil used for par-frying, because it is a relatively expensive raw material. Besides cost reduction, a decrease in oil content would be desired from a nutritional point of view as well, as oil contributes considerably to the caloric value of the product. Furthermore, costly environmental measures are necessary to reduce the emission of vapours from the fryer.

Therefore, in this thesis a fundamentally new concept for the production of par-fried frozen French fries is proposed. The aim was to develop a new, oil-free process, in which superheated steam is used to replace pre-drying and par-frying, and vacuum cooling is used for cooling and freezing. In this way energy use and environmental costs can be reduced considerably. Changing the process conditions may, however, have a strong impact on the product quality. A description of the development and evaluation of this new process is given in Chapter 2. In Chapter 3–7 a new look into the quality aspects of French fries is presented using state-of-the-art equipment. In Chapter 3 crust formation is studied more in detail. Chapter 4 reports identification and olfactometry of flavour compounds extracted from French fries. The real time release of some of these compounds *in vivo* and *in vitro* is studied in Chapter 5. The effect of the new process on flavour release is discussed in this chapter as well. In Chapter 6 a kinetic model is proposed for the formation of acrylamide in a reaction system. In Chapter 7 lipid oxidation is studied at frying conditions. A general discussion of the results obtained is given in Chapter 8.

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Chapter 2

Development and evaluation of a new energy efficient process for French fries production

This chapter has been submitted for publication by WAM van Loon, JPH Linssen, A Legger, RMH Heijmans, HC van Deventer, MJM Burgering, BL van Drooge, and AGJ Voragen.

ABSTRACT

A new, energy efficient production process for French fries was developed and evaluated. Superheated steam (SHS) was used for evaporation of water instead of pre-drying with air and par-frying with oil. The product was frozen by vacuum cooling. Unfortunately, with this process it was not possible to reach the quality of conventional French fries. Sensory analysis indicated that the main quality defect was a tough crust with a fatty appearance. Confocal Scanning Laser Microscopy showed that this was caused by skin formation on the surface during both SHS drying and vacuum cooling. A frying step was necessary to obtain a porous crust. A satisfactory product quality was feasible after drying with SHS instead of air. Due to the concessions made for the product quality, the final energy reduction was limited.

2.1 INTRODUCTION

Manufacturing of French fries started in the middle of the 19th century in the kitchen [1] and has grown to a large-scale industry. Through the years cost reduction and quality improvement have been achieved by transition from batch to continuous production and by optimising unit operations.[2,3] However, the current process still has some disadvantages. The energy use, mainly for evaporation of water and freezing, is high. Furthermore, oil is a relatively expensive raw material that has a strong influence on the caloric value of the product. A high intake of oil is a major health concern. Additionally, costly environmental measures are necessary to reduce the emission of vapours from the fryer.

Superheated steam (SHS) is known to be a very energy efficient drying medium.[4,5] It has found an increasing number of applications in the food industry in the last decades.[6] SHS acts both as heat source to warm up the product and as drying medium to take away the evaporated water from the product. The product surface temperature quickly rises to the boiling point of water at the local pressure and remains at this temperature during the constant rate drying period. When the product starts to dry out at the surface, the falling rate drying period begins, and the surface temperature will rise and finally reach the SHS temperature. By varying pressure, steam temperature, and flow, the drying process and the final moisture content can be controlled in a narrow range.[7] Other advantages, besides the energy efficiency, are that the system is closed and without air, preventing odour emission, oxidation, and the risk of explosion or fire. Disadvantages include the high product temperature (100 °C at atmospheric pressure) for heat sensitive products and additional devices are required for loading and unloading of the product.[8] By applying lower pressures, lower product temperatures will result, but this imposes higher demands on the equipment used.[7] Drying of potato slices with SHS has shown some advantages in comparison with hot air drying with respect to colour and texture.[9-11]

Vacuum cooling is a rapid evaporative cooling technique that can be applied to various food products.[12] The principle is that by reducing the pressure, evaporation of water is accelerated. The heat for evaporation is removed from the product, causing it to cool.[13] When the applied

pressure is low enough, it is possible to freeze the product. This technique is especially suitable for products with a high surface to volume ratio such as leafy vegetables.[12]

This paper presents the development and evaluation of a fundamentally new concept for French fry manufacture. The aim was to reduce environmental and energy costs considerably, while keeping the quality equal to that of the conventional process. In the new process SHS drying will be used for evaporation of water, and vacuum cooling for cooling and freezing.

2.2 MATERIALS AND METHODS

Process description

A schematic overview of the conventional and new process is given in Figure 2.1.

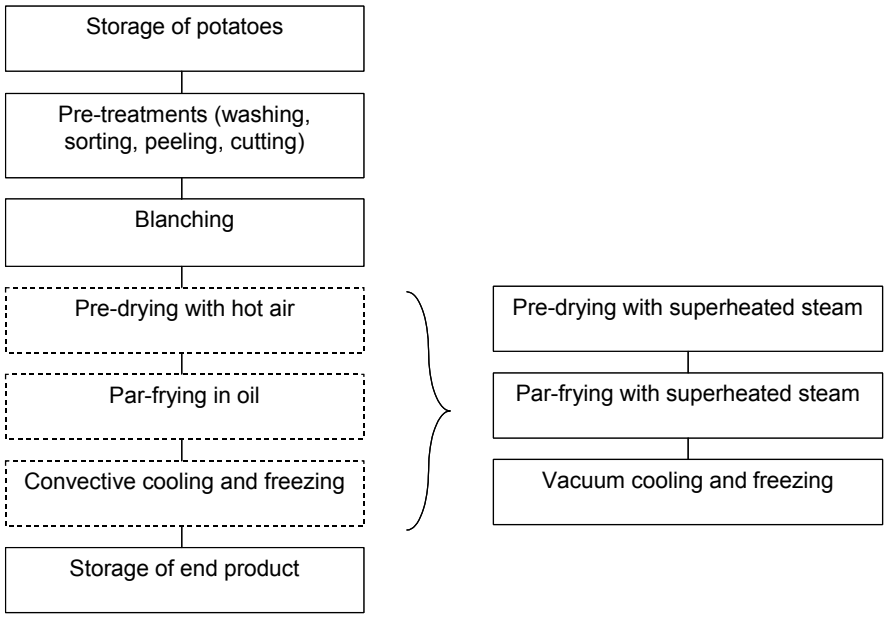

Figure 2.1. Conventional (left) and new process (right) for the production of French fries.

The process steps pre-drying in hot air and par-frying in oil were replaced by a treatment with SHS, and vacuum cooling was used for cooling and freezing. The first part of the process including blanching remained unchanged. Although some functions of blanching such as enzyme inactivation and texture formation could be realised with SHS, blanching in hot water remained necessary to leach out reducing sugars. Reducing sugars react in the Maillard-reaction and are responsible for the development of colour and flavour. Too high amounts will result in a too dark product.[14]

The reduction in energy use was achieved in several ways. SHS can be re-used, and the latent heat of evaporated water from the product can be recovered.[15] Furthermore, vacuum cooling is much more energy efficient than convective cooling systems.[12] By definition water evaporates during vacuum cooling, and therefore less water needs to be removed during the SHS treatment. Another advantage is that there is no emission of odours, because it is a closed system. The steam-drying pilot used for the experiments was described previously by Van Deventer *et al*.[7] A schematic layout of the system is given in Figure 2.2.

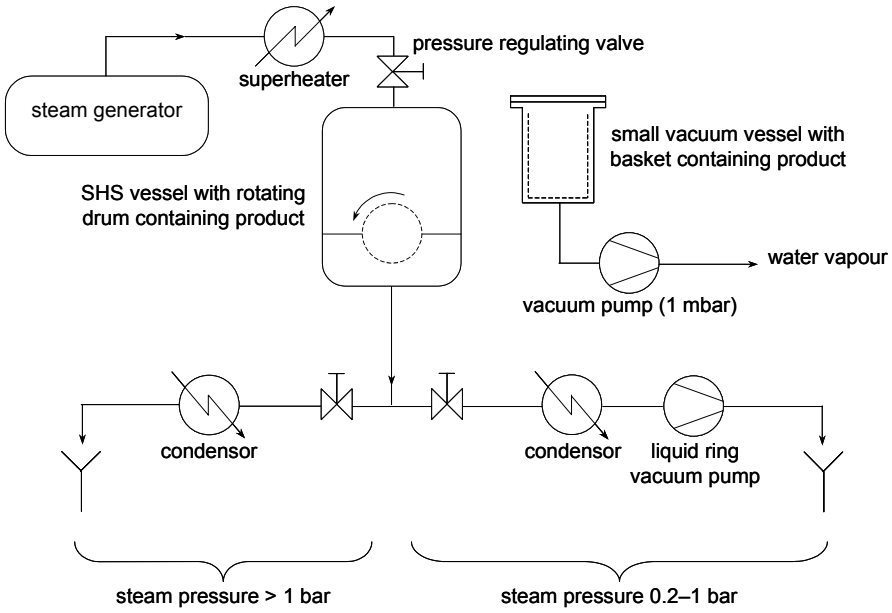

Figure 2.2. Schematic layout of steam-drying pilot.

An additional pump was installed to make operation at low pressure (0.2–1 bar) possible, and a separate vessel was used for vacuum cooling experiments. SHS enters the drying vessel at the top inlet and passes through or around the product. A porous rotating cylinder, coated with Teflon to prevent sticking, was used to ensure a homogenous treatment of the product. Slightly superheated steam leaves the vessel at the bottom outlet and is condensed. Two routes can be chosen depending on the desired pressure. In contrast with the actual SHS process, steam is not recycled.

Sample preparation

Potatoes (variety Agria) were washed and peeled by an abrasive peeler. Potatoes with high dry matter content were selected with a salt solution (1070 kg/m^3, 9.9% w/w NaCl), and floating potatoes were removed. Potatoes were cut to 10 × 10 mm with a table-size manual cutting device and slivers were removed. The strips were weighed in air and under water to determine the dry matter content. After every process step the product was weighed and the moisture loss could be calculated from the assumption that the absolute amount of dry matter remained constant during the process. The strips were subsequently blanched according to standard process conditions in order to inactivate the enzyme polyphenol oxidase and to leach out excess reducing sugars. To obtain a light, homogenous colour, the strips were immersed for 1 min in a 0.4% w/w sodium pyrophosphate solution at 68 °C. Subsequently, the potato strips were transferred into the porous cylinder for the SHS treatment.

Steam temperature, pressure, flow, and residence time were varied over a wide range. The product temperature is (in the constant drying period) equal to the boiling point of water at the local pressure in the vessel.[5] In preliminary experiments the effect of SHS drying was tested independently of the effect of vacuum cooling. Therefore, the product was cooled and frozen in the conventional way: first cooling in a fridge to about 15 °C and subsequently freezing to –18°C in a freezer. Both the fridge and the freezer were equipped with a fan to accelerate the process. Freezing has to take place rapidly, especially in the range 0 to –10 °C, otherwise large ice crystals may form causing damage of the product.[2]

Vacuum cooling and freezing were carried out in two steps. After the SHS treatment, the product was cooled to about 15 °C by lowering the pressure to 10 mbar, and frozen to –18 °C by lowering the pressure to 1 mbar. Three thermocouples were put in the centre of potato strips to register the temperature. A mass and energy balance model was developed to calculate the expected water evaporation during vacuum cooling and freezing. The calculations were used to estimate the processing time during SHS treatment, in order to obtain samples with the desired final moisture content.

All samples were stored in the freezer at –18 °C. Finish-frying was done for 3 min at 180 °C in partially hydrogenated vegetable oil. Industrially produced par-fried, frozen French fries from the same variety and with the same cutting size were used as a reference for the conventional process.

Sensory analysis

Two different panels were used to evaluate the product quality. An analytical panel was used during the development of the process to track down major quality defects. An expert panel was used to test whether the product quality of the final process design could comply with the industrial standard. The analytical panel consisted of twelve assessors that were selected based on their motivation, creativity, availability, and ability to distinguish tastes and odours. Quantitative Descriptive Analysis was used to evaluate the French fries.[16] Three training sessions were carried out to make assessors acquainted with the procedure and the product, and also to generate attributes. In a discussion consensus was reached as to which attributes were most important for the quality of French fries (Table 2.1). During the evaluation assessors were asked to put a mark for all products on each attribute on a 150 mm line scale using a computer program written in Pascal. Scores were calculated by measuring the distance in mm from the left anchor point, and results were evaluated statistically using General Linear Model in SPSS 10.0.7. Differences between products were determined by calculating simple contrasts with the industrial French fries as the reference. Z-values $\geq |2|$ were considered as outliers, and differences were significant at $\alpha \leq 0.05$.

Table 2.1. Attributes used for sensory evaluation with the analytical panel and the expert panel.

Analytical panel	Expert panel
Colour	Colour
Glossiness	Toughness
Crispiness	Crispiness
Amount of filling	Amount of filling
Mealiness of filling	Mealiness of filling
Fatty taste	Taste
Potato taste	Blisters before finish-frying
Doneness	Colour before finish-frying

The expert panel consisted of twelve assessors working at an industrial French fry manufacturer, who are used to evaluate the quality of French fries on a daily basis. The attributes (Table 2.1) and scoring method of the industry were used to evaluate the products. Scores were between 4 (not acceptable) and 8 (very good). Statistical evaluation was the same as with the analytical panel.

Analytical methods

Moisture and oil content were determined in duplicate before and after finish-frying. A lot of moisture evaporates from the French fries during cooling after finish-frying. Therefore, samples were frozen by immersion in liquid nitrogen for 20 s directly after finish-frying and stored at –18 °C until analysis. Moisture content was determined by a standard oven drying method. About 100 g of sample was cut in pieces (< 0.5 cm^3), and a representative 5 ± 0.2 g was weighed and dried to constant weight at 105 °C. Oil content was determined by Soxhlet extraction using the Gerhardt Soxtherm (Dijkstra Vereenigde BV, Lelystad, The Netherlands). About 100 g of sample was cut in pieces (< 0.5 cm^3), and a representative 5 ± 0.2 g was used for the analysis. In the Soxtherm the sample was immersed in boiling petroleum ether for 15 min. Subsequent extraction for 1 hour was enough to extract the total oil from the sample. After extraction petroleum ether was removed with a rotary evaporator and the samples were placed in an oven at 70 °C for 15 min to remove any residual solvent. Samples were cooled to ambient temperature in a desiccator and weighed to calculate the oil content.

Microscopic analysis

Imaging was performed using a Confocal Scanning Laser Microscope type TCS-SP (Leica Microsystems, Rijswijk, The Netherlands), configured with an inverted microscope, and an ArKr laser for single-photon excitation. Cross-section coupes of about 2 mm were cut from a frozen French fry with a sharp razor blade, and stained with a few droplets of a 0.1% solution of FITC (fluorescein isothiocyanate). The coupes were covered with a moisturised cap until analysis to prevent dehydration. A 488 nm laser line was used for excitation, inducing a fluorescent emission of FITC detected between 500–650 nm.

Calculation of energy use

Calculations of the energy use were based on mass and energy balances of the selected process steps. The starting material for the calculations were blanched potato strips (6 × 10 × 10 mm) with a moisture content of 80%, and an initial temperature of 60 °C, because the new and conventional process differ only after blanching. The conventional process was based on a production of 1000 kg/h end product containing 68% of water, 5.5% of oil, and 26.5% of oil-free dry matter. The process steps included pre-drying, par-frying, cooling, and freezing. Air of 80 °C was used at 2.5 m/s to dry the product from 80 to 78% moisture content. During par-frying at 180 °C, the moisture content decreased to 70% and the oil content increased to 5%. Conventional cooling and freezing usually takes place in three steps: cooling with outside air to about 45 °C, mechanical cooling with air of 0 °C to about 10 °C, and freezing with air of –25 °C to –18 °C. Especially during the first cooling step evaporative cooling plays a role, and the moisture content decreases to the final 68%. In the (oil-free) new process the amount of dry matter was kept equal to the conventional process, resulting in a production of 945 kg/h end product, containing 72% of water and 28% of dry matter. The optimal parameters of individual process steps were used in the calculations.

Power consumption of pre-drying and par-frying was based on industrial figures. For cooling and freezing power consumption was calculated using direct expansion of NH_3 (COP = 3.8 for cooling and 2.0 for freezing). Calculation of conventional pre-drying and par-frying showed good agreement with industrial energy consumption.

2.3 RESULTS AND DISCUSSION

Experiments at atmospheric pressure or higher

In the first trials a pressure of 1.0–1.5 bar (product temperature 100–110 °C) was chosen for the SHS treatment. In this way the latent heat of the evaporated water could be recovered at high temperature, and the energy efficiency would be maximised. Unfortunately, the product was cooked so rapidly (after 3 and 5 min for 1.5 and 1.0 bar respectively) that the desired moisture loss could not be reached. Increasing the steam temperature to accelerate drying resulted in blisters on the surface of the potato strips.

Experiments at low pressure

By reducing the pressure, the product temperature decreases, and the product got done slower. Many experiments were carried out to optimise pressure, steam temperature, residence time, and flow to obtain a product with desired internal texture as well as desired moisture content. SHS drying for 13 min at 0.7 bar (product temperature 90 °C) with a steam temperature of 180 °C, and a flow of 100 kg/h was found to be the optimal setting. However, the textural properties of the French fries crust were unsatisfactory. After finish-frying, the crust was tough and the surface showed a fatty appearance. To improve the textural properties, a new approach was chosen. Similar to the conventional process, where the product is first pre-dried in air and subsequently par-fried in oil, the SHS treatment was split up in two parts: a mild step for drying and an intensive step for “frying”. Again, many experiments were performed to optimise the process parameters. The optimised product was offered to the analytical panel together with the reference and with a product treated with SHS in one step (Table 2.2). The results of the sensory evaluation are given in Figure 2.3.

Table 2.2. Process parameters for sensory evaluation with the analytical panel.

Parameters [A]	Moisture content (%) [B]		Oil content (%) [B]	
	par-fried	finish-fried	par-fried	finish-fried
Two step SHS drying				
0,2 bar (60°C) - 110°C - 15 min - 30 kg/h	71.3	54.9	< 0.1	7.0
and 1,5 bar (110°C) - 200°C - 2,5 min - 170 kg/h				
One step SHS drying				
0,7 bar (90°C) - 180°C - 13 min - 100 kg/h	70.8	55.8	< 0.1	6.4
Conventional				
pre-drying in air, par-frying in oil	67.8	52.8	4.7	10.0

[A] pressure (product temperature) - steam temperature - time - flow

[B] Mean of duplicates

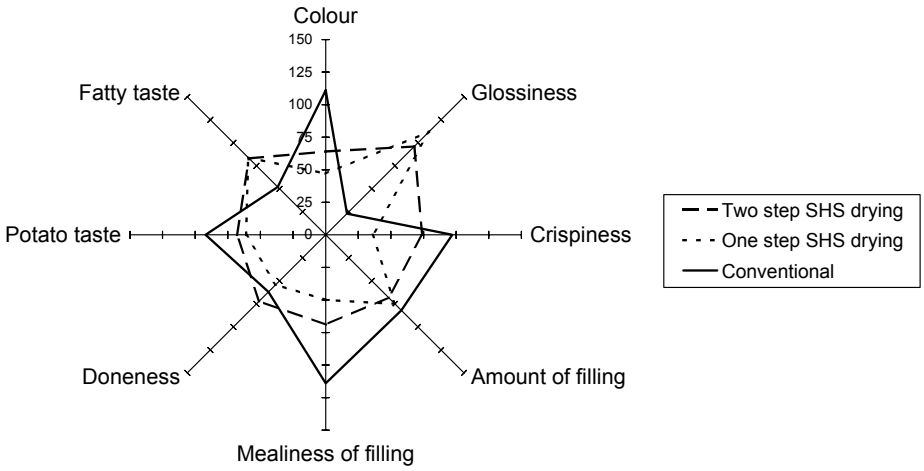

Figure 2.3. Spider web diagram of sensory evaluation with the analytical panel (scale 0–150).

Although the SHS treatment in two steps had an improved crispiness compared to the SHS treatment in one step, the crispiness of the reference was significantly higher. Still, the surface showed a fatty appearance with the two-step SHS treatment after finish-frying, resulting in a significantly higher score for glossiness. Moreover, both SHS treated samples had a higher score

for fatty taste than the reference, while their oil content was in fact lower. It seemed that the SHS treatment formed a skin on the potato strip surface that had a negative influence on the quality of the end product.

Analysis of skin formation

Skin formation on a macroscopic scale is shown in Figure 2.4.

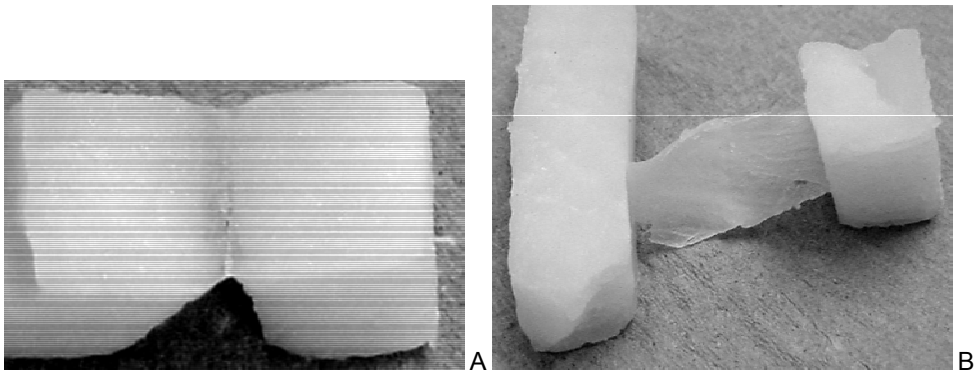

Figure 2.4. Examples of an initial (A) and advanced skin (B) after SHS treatment.

An initial skin, formed during a mild SHS treatment (Figure 2.4A), holds the potato strip together when it is broken, while an advanced skin, formed during an intensive SHS treatment (Figure 2.4B), can be entirely taken from the strip. In fact, skin formation is a known phenomenon in the French fries industry that occurs with excessive pre-drying.[2] Based on the sensory evaluation and observations during the SHS treatment and finish-frying, the following theory about skin formation was proposed (Figure 2.5).

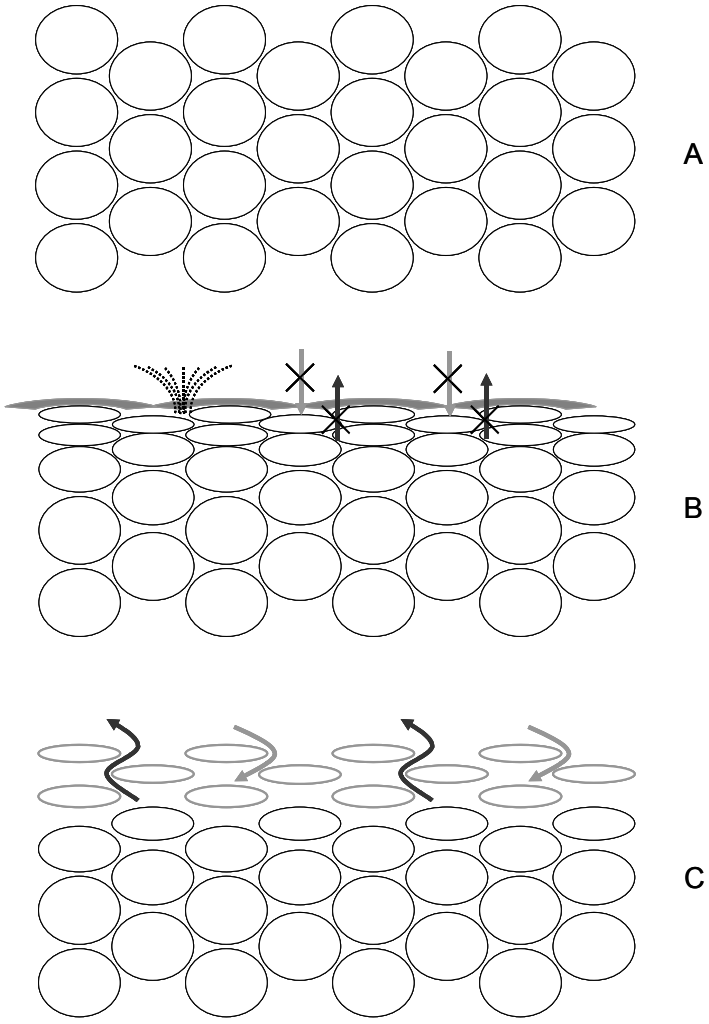

Figure 2.5. Schematic overview of a French fry after blanching (A), during finish-frying with skin (B) and during finish-frying with crust (C): cells are represented by ovals, arrows show the direction of oil (grey) and water vapour (black).

During the SHS treatment water evaporates from the product. In the beginning this is only surface water, but starting at a moisture content of about 75% the surface begins to dry out.[15] Water is transported from the core to the surface because of the concentration gradient. If

evaporation from the surface is higher than transport to the surface, the outer cell layers will dehydrate and a skin is formed. During finish-frying in oil the water transport is hindered, causing pressure to build up until the skin breaks at its weakest point, and vapour is released rigorously (Figure 2.5B). After finish-frying, oil cannot enter the crust and this results in the fatty appearance. In the initial stage of par-frying in oil (Figure 2.5C) only free and capillary water is evaporated from the outer cell layers. The surface dries out fast and a vaporisation region is moving inwards.[17,18] The resistance to the release of water vapour increases and this leads to pressure build-up below the surface. Water vapour is released by the bursting of a few localized sites that break under the stress caused by pressure, resulting in a porous structure.[19] After frying, oil enters the crust because of the capillary pressure difference and the interfacial tension between the oil and the gas within the pores.[20] The effect of SHS drying and par-frying in oil was observed with Confocal Scanning Laser Microscopy (Figure 2.6).

The images support the theory about skin formation. The SHS treatment results in a layer of dehydrated cells in a compact structure (Figure 2.6B). The treatment was so intensive that the skin came loose from the surface. Conventional par-frying in oil gave a porous structure (Figure 2.6C) in which water vapour could escape through open spaces between cells and oil could absorb. As Pedreschi and Aguilera showed previously,[21] cells remain intact in spite of the hard stresses to which the cells were exposed. The heat transition coefficient of oil is about 350 W/m^2K at 165 °C,[22] while the value of SHS at the conditions used for the sensory experiment in Table 2.2 was calculated at 62 W/m^2K. This means that the evaporation is much slower and the pressure build-up during the SHS treatment is insufficient to create a porous cell structure. As no water is left between the cell layers of the skin, the layers cannot be separated during finish-frying. Finally, the built-up pressure causes the skin to burst on a few locations, but the layer still covers most of the French fry. A few cell layers of skin seemed to be enough to affect crispiness and oil absorption significantly. It seems that a frying step is necessary to assure a porous surface and a crispy product.

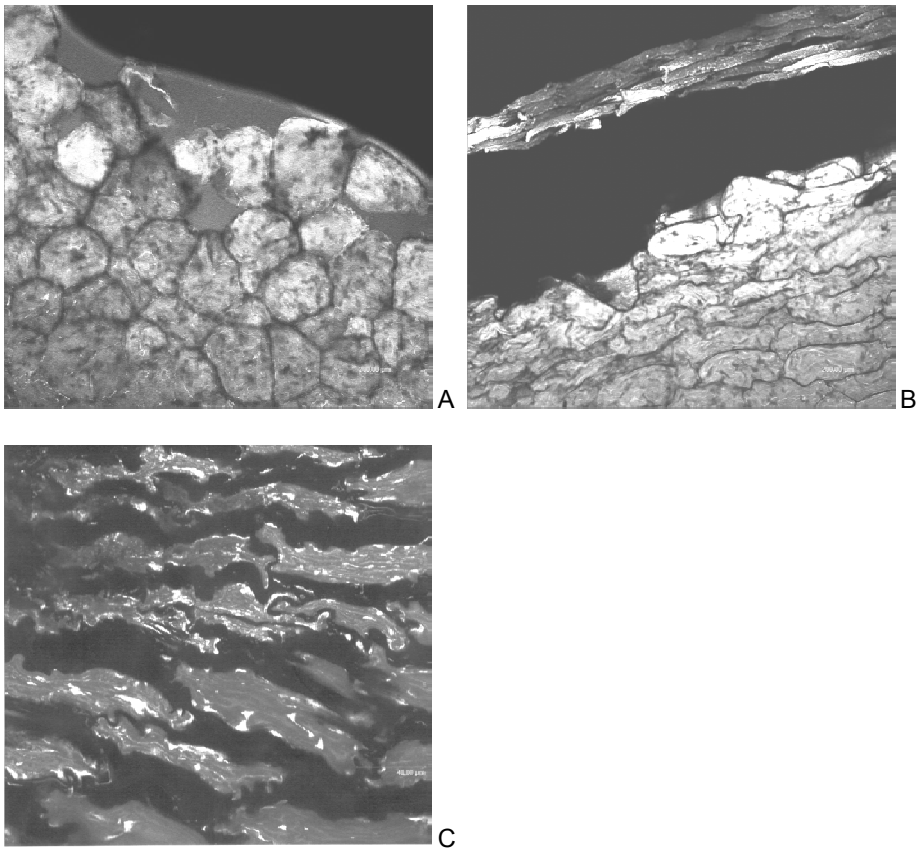

Figure 2.6. CSLM imaging of a French fry after blanching (A, 100x enlarged), after a very intensive SHS treatment (B, 100x enlarged) and after par-frying in oil (C, 200x enlarged).

Vacuum cooling and freezing

Many experiments were carried out with vacuum cooling and freezing, and a selection is shown in Table 2.3.

Table 2.3. Results of experiments with vacuum freezing.

Parameters [A]	Freezing time to –15°C	Final temperature	Remarks
blanched only	6 min	–20 °C	frozen
0,7 bar (90 °C) - 140°C - 10 min - 100 kg/h	> 60 min	–2 °C	soft, not frozen
1,3 bar (107 °C) - 190°C - 1,5 min - 170 kg/h	> 60 min	0 °C	soft, after finish-frying limb and tough
0,2 bar (60 °C) - 105°C - 2 min - 50 kg/h	16 min	–17 °C	frozen, after finish-frying limb and tough
0,2 bar (60 °C) - 110°C - 10 min - 50 kg/h and 1,3 bar (107 °C) - 200°C - 2 min - 170 kg/h	> 60 min	–2 °C	soft, after finish-frying limb and tough

[A] pressure (product temperature) - steam temperature - time - flow

When blanched potato strips are first cooled down to room temperature, vacuum freezing took place rapidly. After a SHS treatment the temperature decline usually stopped around 0 °C, and the product was limb and tough after finish-frying. Evaporation of water is a requirement for this principle of cooling and freezing,[12] but the transport of water from the core to the surface is very slow at low temperature. Although the moisture content was more than 70%, apparently not enough water was available at the surface. The amount of water evaporating during vacuum cooling and freezing was calculated to be 75% of the amount of water that was removed in the whole process. This means that in the SHS treatment the moisture content had to decrease from 80% to 78.4%. A very mild SHS treatment is sufficient (0,2 bar - 105 °C - 2 min - 50 kg/h), but unfortunately the product quality was not acceptable due to skin formation.

From the experiments with SHS it was concluded that a traditional frying step is required to obtain a porous crust. A porous structure might facilitate vacuum freezing. Frying for 15 s at 165 °C resulted in the same decrease of moisture content as the very mild SHS treatment. Vacuum cooling after this short frying step to about 20 °C took about 10 min. Vacuum freezing was, however, not successful. The product temperature did not even reach 0 °C, but stopped at 5 to 10 °C. Probably, the layer of oil on the outside hindered water transport, especially when the oil started to solidify.

Evaluation of new process

The design of the new process changed considerably during the development. Vacuum freezing was not possible, and a frying step was necessary because of the product quality. Two remaining process routes were evaluated by the expert panel: SHS pre-drying - par-frying in oil - vacuum cooling - conventional freezing, and SHS pre-drying - par-frying in oil - conventional cooling and freezing (Table 2.4). The results of the sensory evaluation are shown in Figure 2.7.

Table 2.4. Process parameters for sensory evaluation with the expert panel.

Pre-drying [A]	Par-frying	Cooling	Moisture content (%) [B]	Oil content (%) [B]
SHS pre-drying + vacuum cooling				
0,2 bar (60°C) - 90°C - 15 min - 50 kg/h	35 s, 165°C	Vacuum, 20 mbar	69.3	2.7
SHS pre-drying + conventional cooling				
0,2 bar (60°C) - 90°C - 20 min - 50 kg/h	45 s, 165°C	Air	68.5	3.0
Conventional				
Air	45 s, 165°C	Air	69.6	3.0

[A] pressure (product temperature) - steam temperature - time - flow

[B] After par-frying, mean of duplicates

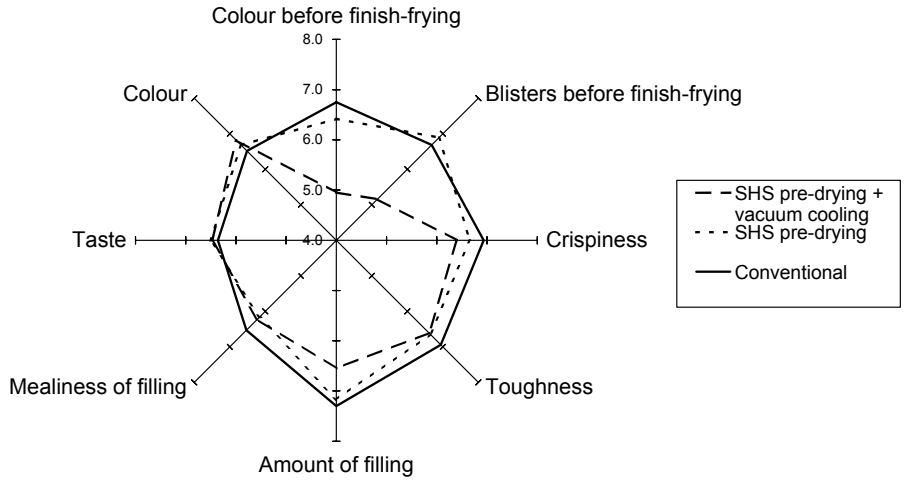

Figure 2.7. Spider web diagram for results of sensory evaluation with the expert panel (scale 4–8).

Replacing pre-drying in air with SHS did not result in significant different quality aspects. Vacuum cooling, however, caused blisters on the surface. The blisters did not affect the product quality to the same extend as skin formation, because crispiness and toughness were not significantly different from the industrial reference. Nevertheless, blisters are considered a major quality defect in the industry.

Energy use of new process

The energy use of the conventional process is set to 1, and the relative energy uses of several process routes are shown in Table 2.5.

Table 2.5. Energy reduction of process routes.

Process route	Pre-drying	Par-frying	Cooling	Freezing	Thermal energy [A]	Electricity [A]
Conventional	Air	Oil	Air	Air	1	1
Conventional + heat recovery	Air	Oil	Air	Air	0.77	1
SHS pre-drying	Steam	Oil	Air	Air	0.58	0.98
SHS pre-drying + vacuum cooling	Steam	Oil	Vacuum	Air	0.48	0.93
Original new process	Steam	Steam	Vacuum	Vacuum	0.35	0.63

[A] Thermal energy and electricity are relative to conventional process (set to 1)

With SHS drying it is possible to recover the latent heat of the water evaporated in the fryer and to use it to heat up pre-drying air. This way of saving energy is already common practice for some manufacturers. The largest energy reduction would have been realised with the original new process including SHS treatments and vacuum cooling and freezing. A process with vacuum cooling and a frying step would still have saved a considerable amount of energy, because part of the water removal would be achieved during cooling. Replacing air with SHS for pre-drying would save about 25% of thermal energy in comparison with the conventional process with heat recovery. Despite the energy reduction and reduced odour emission, the financial savings are small in comparison with the high investment costs for the SHS drying equipment (return on investment is about 9 years).

2.4 CONCLUSION

The new production process including SHS treatment and vacuum freezing did not result in good quality French fries. The main problem was skin formation on the surface resulting in a tough product with a fatty appearance. A frying step was necessary to obtain a porous and crispy crust. The only aspect of the new process that did not influence the product quality was replacing air by SHS for pre-drying. Due to the concessions made for the product quality, the final energy reduction was limited. Therefore, the conclusion was drawn that this promising, innovative process offered insufficient economic perspective. However, an enormous increase of insight was obtained about processes that occur in French fries on micro-scale, and how process conditions influence product quality.

2.5 ACKNOWLEDGEMENTS

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Chapter 3

Effect of pre-drying and par-frying conditions on the crispness of French fries

This chapter has been submitted for publication by WAM van Loon, JE Visser, JPH Linssen, DJ Somsen, HJ Klok, and AGJ Voragen.

ABSTRACT

An experimental design was used to study the effect of pre-drying (to 10, 15, and 20% weight loss) and par-frying conditions (160, 170, and 180 °C) on the crispness of French fries. Par-frying time was adjusted with a software program to obtain equal moisture content and internal texture for all samples. Crispness was evaluated with a sensory panel, with a Texture Analyser, and with Confocal Scanning Laser Microscopy (CSLM). Par-frying at 180 °C resulted in a crispier product than at 160 and 170 °C. Pre-drying to 20% weight loss lead to blisters and reduced crispness in comparison with pre-drying to 10 and 15% weight loss. Instrumental texture measurements showed a good correlation with sensory crispness. Large differences in cell structure, such as blisters, could be observed with CSLM. CSLM was useful to explain results from the instrumental and sensory texture evaluation.

3.1 INTRODUCTION

French fries are appreciated throughout the world because of their pleasant taste and texture.[1] The general process for French fries production is blanching-drying-frying and each step is important for the final product quality.[2] Furthermore, the process requires permanent adjustment according to the raw material characteristics and the interrelations among the process steps.[3] Blanching in hot water is used mainly to inactivate enzymes, to improve texture, and to obtain a bright, uniform colour.[4] Pre-drying prior to the frying step improves texture and reduces oil uptake.[5] Oil absorption is reduced in two ways. Firstly, the proportion of open pores is decreased during pre-drying due to shrinkage.[6] After frying, oil is taken up in the open pores from which water has evaporated.[7] Decreasing the volume of open pores will reduce oil uptake. Secondly, pre-drying is responsible for part of the moisture loss, and, therefore, the frying time can be shortened.[5] Generally, frying is a two-step procedure: par-frying and finish-frying. During par-frying part of the water is evaporated and crust formation starts. After par-frying the product is frozen, packaged, and distributed. Finish-frying takes place in a restaurant or at home shortly before consumption, and results in the final product with the desired flavour and texture.

Frying is an operation, in which mass and heat transfer take place simultaneously.[8] During frying the product characteristics change considerably. Heat is transferred from the oil to the product, and water is evaporated from the product surface in the form of steam bubbles. In the beginning this is only free water, but as the surface dries out a boundary of evaporating water is moving inwards.[3] The temperature at the boundary does not exceed 103 °C.[9] A crust is formed, which increases the resistance to water vapour transport, and causes an increase in pressure in the surface area.[10] The product only shrinks in the first stage of the frying process (by 5–10%); afterwards the size stabilises, while the crust thickness and the porosity increase upon further frying.[5] Oil uptake into the product occurs mainly after frying, when the product is removed from the oil, by both condensation and capillary mechanisms.[11]

The texture of French fries consists of two parts: a crispy outer crust and a soft, mealy interior.[12] The interior of French fries consists of cooked and slightly dehydrated cells,[13] and the texture is similar to cooked potatoes. Microscopic analysis of potato strips, fried in dyed oil, showed that

the oil is located in the crust region only.[14] The crust has a thickness of about 1 mm, depending on the frying time and temperature. In a structural sense, the crust can be considered a semi-rigid sponge, filled with oil, and about 80% of the crust's volume is made up of void space.[15] Pedreschi and Aguilera [16] used Confocal Scanning Laser Microscopy (CSLM) to show that oil in the crust was like an "egg-box" surrounding intact dehydrated potato cells, but did not penetrate into them.

Crispness is an important quality attribute of French fries, and it depends to a large extent on the crust properties. Crispness is usually determined with a sensory panel, but this is a time consuming procedure. Texture analysers are generally used as an instrumental alternative to predict crispness in an objective way. Several physical parameters derived from a force-deformation curve showed a good correlation with sensory crispness.[17,18] These include distance at maximum force, initial slope, maximum force divided by distance, and area below the force-deformation curve. A better relationship between structure and texture was, however, found by studying the jaggedness of the force-deformation curve.[19] The jaggedness of the curve corresponded with the many breaking events that occur by puncturing a crispy material. Visser *et al*.[20] recently developed a new method to study the jaggedness of force-deformation curves obtained from several solid cellular crispy foodstuffs. The number of peaks in a force-deformation curve during fracture was used as a measure for crispness, and a good correlation with sensory perceived crispness was found for the tested foodstuffs.

The moisture content has a significant effect on crispness.[17,21] Also, the internal texture of the product can affect textural properties of the crust.[22] These aspects have, however, often been neglected when determining the crispness of French fries. A higher value for crispness was found in French fries with increased drying time [23] and also with increased frying time.[24] It was, however, not clear whether this could be attributed to the varied condition or to a difference in moisture content. Therefore, in the present research the effect of pre-drying and par-frying conditions on crispness of French fries was studied independent of the moisture content and internal texture. To achieve this, the frying time was adjusted in such a way that the moisture content and internal texture were equal for all samples. Crispness was evaluated in three different ways: sensory with a panel, instrumentally with a Texture Analyser, and microscopically with CSLM.

3.2 MATERIALS AND METHODS

Sample preparation

Lab-scale equipment at Aviko BV (Steenderen, The Netherlands) was used for sample preparation.[25] Potatoes from one batch (cv. Agria, 21.9% dry matter) were used throughout the study to minimise variation in raw material. For each experiment 3 kg of potatoes were peeled for 25 s at 16 bar with a steam peeler, and cut into strips (11 × 11 mm) with a mechanical cutting device. Subsequently, the strips were blanched in 50 l of blanching water from the factory according to standard blanching conditions. In this way starch was gelatinised and a desired proportion of reducing sugars was leached out. After blanching the strips were dipped in a 0.5% solution of sodium pyrophosphate in blanching water (40 s at 70 °C) in order to obtain a bright and uniform colour. Table 3.1 shows the experimental design that was used to determine the effects of pre-drying (10, 15, and 20%) and par-frying (160, 170, and 180 °C). A full factorial design was set-up in triplicate, and the experiments were carried out in randomised order. Pre-drying was carried out in hot air (70 °C). The extent of pre-drying was expressed as the percentage of weight loss:

$$M_{\text{after pre-drying}} = M_{\text{before pre-drying}} * (100 - \text{drying percentage}) / 100)) \quad (3.1)$$

The par-frying time was chosen in such a way that all samples had the same final moisture content and internal texture. This was calculated using a software program developed at Aviko BV, which was based on extensive previous research. In fact, this means that the effect of different time-temperature combinations of par-frying was studied, instead of different par-frying temperatures. Unhardened palm oil was used for par-frying in a product to oil ratio of about 1:13. After par-frying, oil was allowed to drain off for 30 s before cooling. The strips were consecutively cooled for 15 min (till 20 °C), chilled for 15 min (till 2 °C), and frozen in 20 min (till –20 °C). For all analyses only straight strips with a length of 5 to 10 cm were used.

Table 3.1. Process conditions of experiments in the experimental design.

Experiment	Pre-drying (%)	Par-frying	
		Temperature (°C)	Time (s)
1	10	160	134
2	10	160	134
3	10	160	134
4	10	170	111
5	10	170	111
6	10	170	111
7	10	180	95
8	10	180	95
9	10	180	95
10	15	160	125
11	15	160	125
12	15	160	125
13	15	170	104
14	15	170	104
15	15	170	104
16	15	180	88
17	15	180	88
18	15	180	88
19	20	160	116
20	20	160	116
21	20	160	116
22	20	170	96
23	20	170	96
24	20	170	96
25	20	180	81
26	20	180	81
27	20	180	81

Sensory evaluation

A panel of three experts with many years of experience (>7 years) in testing French fries evaluated the samples. They judged the samples on crispness, blisters, colour, and two attributes for internal texture: homogeneity and doneness. The panel used a scale from 4 to 8 for the

evaluation and the use of half and quarter points was permitted. Together they agreed on one score per attribute and sample. In order to limit the amount of samples per session, three samples were evaluated in one session.

Texture analysis

A Texture Analyser (TA-XT Plus, Stable Micro Systems Ltd., Surrey, UK) was used for instrumental analysis of the French fries samples. A standardised protocol was followed for each analysis. Samples were finish-fried individually for 3 min at 180 °C, and after finish-frying oil was allowed to drain off for 30 s. Texture analysis was performed exactly 3 min after the sample was removed from the fryer. The French fry was fractured longitudinally with a wedge-shaped probe (30° cutting angle, 15 mm width) at a speed of 40 mm/s. This simulated a bite with the front teeth.[26] Ten replicates were carried out of each sample.

A force-deformation curve was constructed from the resistance that the probe encountered during penetration. Because the peaks in the diagram have a very short timescale, a high acquisition rate of 65000 Hz was used to register all peaks. An example of a force-deformation curve is shown in Figure 3.1.

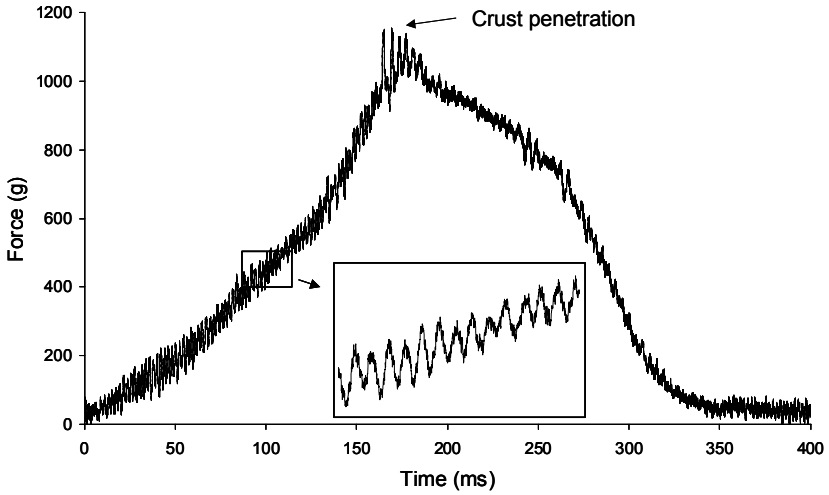

Figure 3.1. Example of force-deformation curve with magnification of peak pattern.

Penetration of the crust occurred within 200 ms after the probe touched the sample surface. Therefore, only this part of the force-deformation curve was used for further analysis. The number of peaks during penetration of the crust was used as a measure for crispness. The number of peaks in the force-deformation curves was counted using the method of Visser *et al*.[20] In this method the number of peaks above a certain threshold value is counted. This threshold value defines the minimum peak size in terms of the difference between the minimum and the maximum force of a peak. Preliminary experiments on samples of French fries showed that a threshold value of 60 g was optimal.

Microscopic analysis

The cell structure in the crust of all samples was observed before finish-frying with a CSLM type TCS-SP (Leica Microsystems, Rijswijk, The Netherlands), configured with an inverted microscope and an ArKr laser for single-photon excitation. A 488 nm laser line was used for excitation, inducing a fluorescent emission of FITC detected between 500–650 nm.[27] Cross-section coupes of about 2 mm were cut from a frozen French fry with a sharp razor blade, and stained with a few droplets of a 0.1% solution of fluorescein isothiocyanate in water. The coupes were covered with a moisturised cap until analysis to prevent dehydration. Additionally, a stereomicroscope type MZ-16 (Leica Microsystems) was used to make images of the product surface.

Determination of moisture and oil content

Moisture and oil content were determined in duplicate before and after finish-frying. Finish-frying was carried out for 3 min at 180 °C, and after this oil was allowed to drain off for 30 s. To minimise moisture loss, samples were frozen by immersion in liquid nitrogen for 20 s, and stored at –18 °C until analysis. A standard oven drying method was used to determine the moisture content. About 50 g of sample was cut in pieces (< 0.5 cm^3), and a representative 5 ± 0.2 g was weighed and dried to constant weight at 105 °C. Fat content was determined by Soxhlet extraction using the Gerhardt Soxtherm (Dijkstra Vereenigde BV, Lelystad, The Netherlands) following the same sampling procedure as described above. In the Soxtherm the sample was immersed in boiling petroleum ether for 15 min. Subsequent extraction for 1 hour was enough to extract the total fat from the sample, and petroleum ether was removed by

evaporation. Samples were placed in an oven at 70 °C for 15 min to remove any residual solvent. Samples were cooled to ambient temperature in a desiccator and weighed to calculate the oil content.

Statistical analysis

All statistical analyses were performed using SPSS 10.0.7. Sensory and instrumental data were evaluated with General Linear Model using pre-drying and par-frying as fixed factors. Z-values ≥ |2| were considered as outliers. Difference contrasts were calculated to determine the significance level of the settings for pre-drying and par-frying. Pearson correlation was used to calculate correlations between sensory and instrumental parameters.

3.3 RESULTS

Sensory evaluation

Table 3.2 shows the results of the sensory evaluation.

Table 3.2. Results of sensory evaluation of French fries samples (line scale 4–8).

	Crispness	Blisters	Colour	Homogeneity	Doneness
Pre-drying [A]					
10%	6.61 ab	7.36 a	7.33 a	6.67 a	5.94 a
15%	6.88 a	6.67 b	7.29 a	6.75 a	6.00 a
20%	6.39 b	5.36 c	7.25 a	6.78 a	5.47 b
Par-frying					
160 °C	6.58 b	6.58 a	7.08 b	6.69 a	5.94 a
170 °C	6.48 b	6.46 a	7.31 ab	6.60 a	5.71 a
180 °C	6.96 a	6.41 a	7.47 a	6.94 a	5.86 a

[A] Different letters are significantly different at $P < 0.1$. Values are averages of all samples pre-dried to 10% (exp. 1-9), 15% (exp. 10-18), and 20% (exp. 19-27) weight loss, respectively.

Significant effects of pre-drying and par-frying on crispness were found. Samples, pre-dried until 15% weight loss were significantly crispier than those pre-dried until 20% weight loss. No

significant difference between pre-drying to 10 and 15% weight loss was found. Par-frying at 180 °C resulted in a significantly higher crispness in comparison to par-frying at 160 and 170 °C. A strong effect of pre-drying on blister formation was found. Linear regression showed a positive relation between the extent of pre-drying and the degree of blisters ($P < 0.001$, $R^2 = 0.84$). Furthermore, significant effects were found for pre-drying on doneness and for par-frying on colour. Pre-drying until 20% weight loss resulted in a significantly lower value for doneness compared to pre-drying until 10 and 15% weight loss. Colour showed the tendency to increase with par-frying temperature, but no statistically significant relation was found ($P > 0.05$, $R^2 = 0.18$). Nevertheless, a significantly better colour was obtained for samples par-fried at 180 °C than at 160 °C.

Texture analysis

Table 3.3 shows the results of the texture analysis.

Table 3.3. Results of texture analysis of French fries samples.

	Number of peaks
Pre-drying [A]	
10%	55.1 a
15%	53.8 a
20%	50.2 b
Par-frying	
160 °C	52.9 b
170 °C	51.0 b
180 °C	56.2 a

[A] Different letters are significantly different at $P < 0.05$. Values are averages of all samples pre-dried to 10% (exp. 1-9), 15% (exp. 10-18), and 20% (exp. 19-27) weight loss, respectively.

Pre-drying until 10 and 15% weight loss resulted in a significant higher number of peaks in the force-deformation curve than pre-drying until 20% weight loss. For par-frying at 180 °C a significantly higher number of peaks was found than for par-frying at 160 and 170 °C.

Microscopic analysis

Figure 3.2 shows a number of typical structures that were observed in the crust of the samples. An overview in which samples blisters and other typical structures were observed is given in Table 3.4.

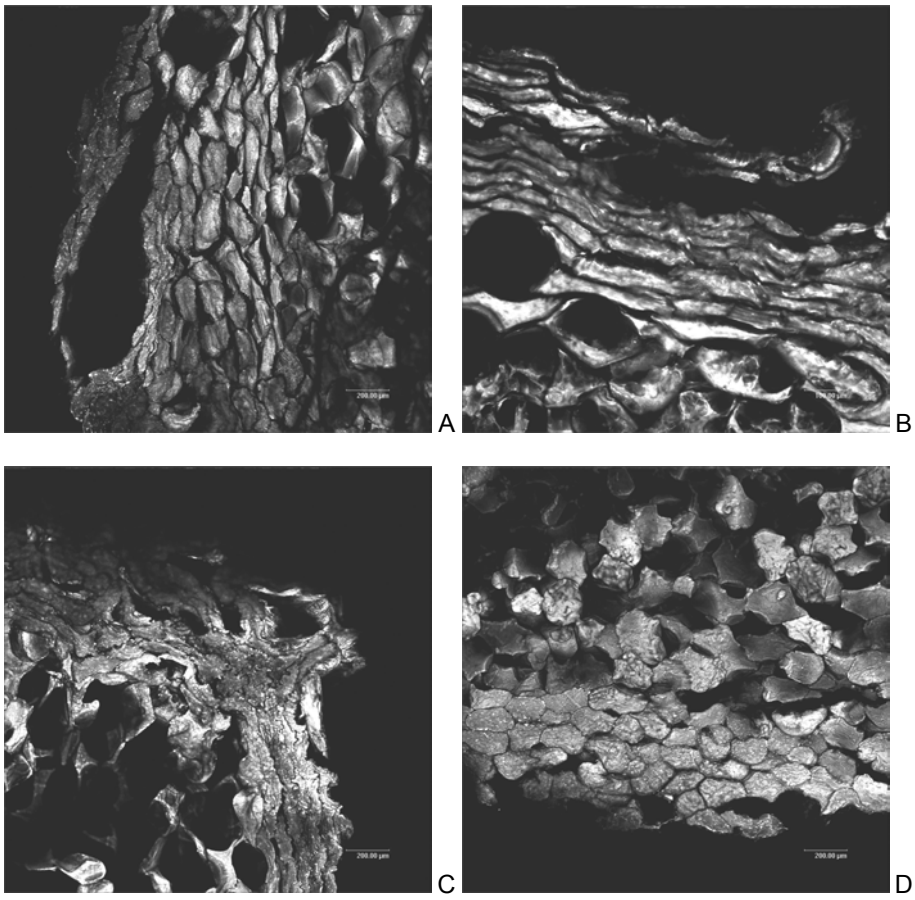

Figure 3.2. CSLM images of typical structures observed in the French fries samples of experiment 21(A), 17 (B), 26 (C) and 2 (D).

Table 3.4. Typical structures observed in CSLM images of French fries samples.

Structure	Description	Experiment [A]
Figure 3.2A	Layer of cells forming an air pocket	19, 20, 21, 25
Figure 3.2B	Flat cells in open structure	4, 7, 12, 14, 17
Figure 3.2C	Flat cells in compact structure	6, 18, 22, 26
Figure 3.2D	"Round" cells until surface	1, 2, 4, 15

[A] See Table 3.1.

The structure in Figure 3.2A looked like a blister, as a layer of cells was separate from the surface forming an air pocket. This was confirmed by stereomicroscopy. Figure 3.3A shows the surface of a French fry with blisters and one without, and Figure 3.3B represents a close-up of a blister.

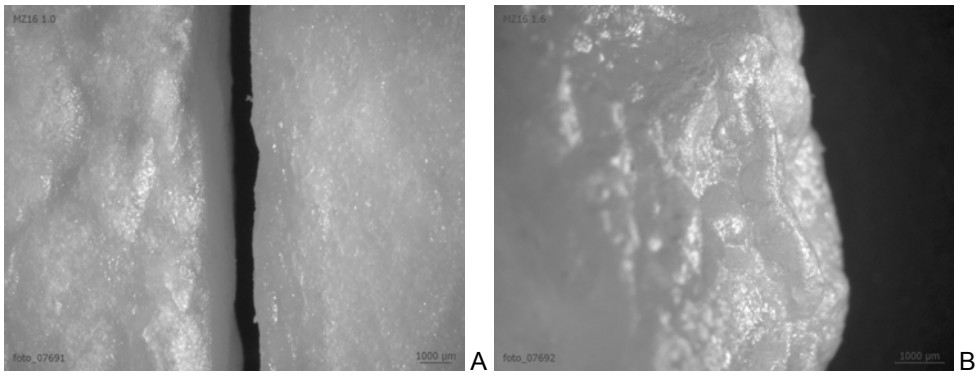

Figure 3.3. Stereomicroscope images of the surface of a French fry with and without blisters (A, respectively left and right), and a close-up of a blister (B).

The open structure of Figure 3.2B was generally found in samples that had a high score for crispness in the sensory evaluation. This included samples that were pre-dried until 10 and 15% weight loss, but not samples pre-dried until 20% weight loss. The structure did, however, not occur more often in one of the time-temperature combinations of par-frying. Most of the samples, in which the structure of Figure 3.2D was observed, had been pre-dried to 10% weight loss. The structure of Figure 3.2C could not be attributed to a specific pre-drying or par-frying

condition. Generally, samples, of which Figure 3.2C and 3.2D are representatives, had a lower score for crispness.

Moisture and oil content

The moisture and oil contents, determined before and after finish-frying, are shown in Table 3.5.

Table 3.5. Moisture and oil content of French fries samples before and after finish-frying.

	Moisture content (%)		Oil content (%)		Oil content (g/g ds)	
	Before finish-frying	After finish-frying	Before finish-frying	After finish-frying	Before finish-frying	After finish-frying
Pre-drying[A]						
10%	66.8 a	52.1 a	4.53 a	9.54 a	0.136 a	0.200 a
15%	66.1 a	52.8 a	4.30 a	9.68 a	0.127 b	0.205 a
20%	67.4 a	53.4 a	3.89 b	8.94 b	0.120 c	0.192 b
Par-frying						
160 °C	67.1 a	52.4 a	4.24 ab	9.41 a	0.128 ab	0.198 a
170 °C	67.0 a	52.5 a	4.13 b	9.25 a	0.125 b	0.196 a
180 °C	66.2 a	53.4 a	4.40 a	9.60 a	0.130 a	0.206 a

[A] Different letters are significantly different at $P < 0.05$. Values are averages of all samples pre-dried to 10% (exp. 1-9), 15% (exp. 10-18), and 20% (exp. 19-27) weight loss, respectively.

No significant effects on moisture content were found. There were, however, effects of both pre-drying and par-frying on oil content. Pre-drying until 20% weight loss resulted in significantly less oil uptake than until 10 and 15% weight loss. The effect was even more apparent when the oil content was expressed on the basis of dry matter. Similar results were obtained after finish-frying. The oil content was significantly higher after par-frying at 180 °C than at 170 °C. The oil content of samples that were par-fried at 160 °C was in between the other temperatures. Expressing the oil content on the basis of dry matter gave similar results. After finish-frying the same trend was observed. The highest oil content was found for samples par-fried at 180 °C and the lowest value for samples par-fried at 170 °C. The difference was, however, not significant after finish-frying.

3.4 DISCUSSION

Significant effects of the extent of pre-drying and of different time-temperature combinations of par-frying on crispness were demonstrated. These effects were independent of the moisture content, as no significant differences in moisture content could be found among the samples. A strong correlation between sensory and instrumental analysis of crispness was obtained ($P < 0.01$, $R^2 = 0.76$). Both sensory evaluation and texture analysis showed that the highest value for crispness resulted from par-frying at 180 °C. In microscopic analysis, however, the typical cell structure associated with a crispy crust did not occur more often in samples that were par-fried at 180 °C than at 160 and 170 °C. The enhanced crispness may be explained by the temperature difference between surface and core. The core temperature remains at 103 °C, because of the presence of water.[3,13] A higher frying temperature, therefore, results in a larger temperature difference and a thicker crust. In the present study it is, however, likely that the frying time compensated this effect to some extent. This would explain why no difference was found between par-frying at 160 and 170 °C. Another explanation for the effect of par-frying at 180 °C is that the pressure build-up of evaporating water in the crust region is larger at this temperature. The cells will be pushed away more vigorously as water vapour forces its way outside, and this will result in a more porous crust structure. Previously, it was shown that porosity of French fries increases with frying temperature.[28] This would also explain the higher uptake of oil that was found after par-frying at 180 °C. Because of a higher porosity a higher amount of oil can be absorbed in the product after removal from the fryer.

Pre-drying until 20% weight loss resulted in the lowest value for crispness in the sensory evaluation and for the number of peaks in the texture analysis. No differences were found between pre-drying to 10 and 15%, although microscopic analysis showed that the structure of "round" cells at the surface occurred mostly at pre-drying to 10% weight loss. Samples pre-dried to 10% weight loss were par-fried for a longer time than samples pre-dried to 15% weight loss in order to obtain equal final moisture contents (see Table 1). Apparently, this compensated each other with respect to crispness. The longer par-frying time resulted in a slightly higher oil uptake, but this was equalised after finish-frying. Krokida *et al.*[23] observed a strong positive effect of pre-drying time on crispness. This effect can, however, be attributed to differences in moisture content to a large extent. Remarkably, they did not report any negative effects of

prolonged pre-drying. Gupta *et al*.,[8] on the other hand, stated that intensive pre-drying has a negative effect on the texture of French fries. This was found in the present study as well, because sensory analysis and microscopic observations revealed that blisters were formed on the product surface after pre-drying until 20% weight loss. It seems, therefore, that there is an optimum in the extent of pre-drying. Pre-drying can be used to partially replace par-frying by removing loosely bound water. As the par-frying time is shortened, the oil uptake will be reduced. However, on prolonged pre-drying the outer cell layers will dry out and skin formation will occur. This has been observed previously in experiments, in which potatoes were dried in hot air.[29,30] During subsequent par-frying, a layer of dried cells will be separated from the cells underneath at several areas forming blisters. Moreover, this layer hinders oil absorption, as the oil content before and after finish-frying of samples pre-dried to 20% weight loss was considerably lower than the other samples and the reference.

Correlation coefficients among attributes from the sensory evaluation are given in Table 3.6.

Table 3.6. Correlations among sensory attributes.[A]

	Crispness	Blisters	Colour	Homogeneity	Doneness
Crispness	1				
Blisters	0.20	1			
Colour	0.52**	0.11	1		
Homogeneity	0.53**	-0.10	0.39*	1	
Doneness	0.22	0.46*	-0.28	-0.01	1

[A] * Significant at P < 0.05; ** Significant at P < 0.01

Significant correlations were found among crispness, homogeneity, and colour. This is probably caused by the high scores of these attributes for par-frying at 180 °C, although the score for homogeneity was not significantly different. The colour significantly improved as the temperature of par-frying increased. The time-temperature combinations used in the experimental design were calculated on the basis of moisture loss and development of internal texture, and colour was not taken into account. Apparently, the time-temperature combination calculated for par-frying at 180 °C was optimal for colour as well. Furthermore, a significant correlation between doneness and blisters was found. Both attributes had a low score for

samples pre-dried to 20% weight loss. This suggests that excessive pre-drying not only causes blisters, but also affects the perceived doneness in a negative way.

3.5 CONCLUSION

Par-frying at 180 °C resulted in a more crispy product than par-frying at 160 and 170 °C. Pre-drying to a weight loss of 20% lead to blister formation having a negative influence on crispness. No difference in crispness was found between pre-drying to 10 and 15% weight loss; a longer par-frying time compensated a lower extent of pre-drying. The number of peaks during fracture correlated well with sensory crispness. Large differences in cell structure, such as blisters, could be observed with CSLM, but it was not possible to show differences in crispness. Nevertheless, CSLM gave insight in the cell structure and this was useful to explain results from the sensory evaluation and instrumental texture analysis.

3.6 ACKNOWLEDGEMENT

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Chapter 4

Identification and olfactometry of French fries flavour extracted at mouth conditions

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ABSTRACT

The aim of this study was to isolate and identify odour active compounds from French fries at mouth conditions. Volatile compounds were released from French fries by purge-and-trap, trapped on Tenax TA, and identified with GC-MS. GC-olfactometry was used to determine odour active compounds with a trained panel using the detection frequency method. A total of 122 compounds were identified of which 85% originated from either sugar degradation and/or Maillard reaction and 15% from lipid degradation, based on relative areas. About 50 odour active compounds were, due to coelution, responsible for 41 odours perceived by the panel. 3-Methylbutanal and 2-methylbutanal, hexanal, 2,3-dimethylpyrazine, 2-methylpropanal, 2,3-butanedione, pyridine, heptanal, 2,5-dimethylpyrazine and/or 2,6-diemethylpyrazine and/or ethylpyrazine, dimethyl trisulfide, octanal, phenylacetaldehyde, 2,5-diethylpyrazine, (*E*)-2-nonenal, 3-methylbutanoic acid and/or 2-methylbutanoic acid, (*E,Z*)-2,4-heptadienal, (*E*)-2-octenal, 5-ethyl-2,3-dimethylpyrazine and/or 2-ethyl- 3,5-dimethylpyrazine, nonanal, and tentatively 2-methylpyrrole had the highest detection frequencies. This resulted in a strong malty and fried potato note, combined with caramel/ buttery, green, spicy, and deep-fried notes. Also chemical and sweaty odours were observed.

4.1 INTRODUCTION

French fries are popular around the world because of their pleasant taste, which is a combination of a crispy crust, soft inside and typical fried potato flavour. The flavour of potato has been investigated extensively. According to a review by Maga,[1] more than 500 volatiles have been identified so far.

The composition of volatiles obtained from major cooking procedures differs significantly.[2] Therefore, a distinction should be made between raw,[3] boiled,[3-6] oven baked,[7-13] microwave baked,[4,14] and French fried potatoes.[15-17] Lipid oxidation is the major source of volatiles in raw potatoes, because the lipoxygenase content is relatively high.[5] In boiled potatoes the concentration of lipid-derived compounds is lower than in raw potatoes. This is either due to degradation during boiling or to less enzymatic activity since shredding is done after boiling, when enzymes are inactivated.[3] The composition of volatiles changes upon heating. The Maillard reaction becomes predominant during oven-baking of potatoes, while a microwave treatment results in a composition of volatiles between boiled and oven-baked potatoes.[4] Duckham *et al*.[7] compared volatiles of oven-baked potatoes from eleven cultivars and classified them by their origin: lipid degradation, sugar degradation and/or Maillard reaction not involving sulfur amino acids, sulfur amino acid degradation, methoxypyrazines, and terpenes. There are great similarities between the composition of oven-baked potatoes and potato chips, but also some notable differences.[2] In fried potato products flavour compounds are not only formed from the potato, but also from the frying oil and from the interaction of Maillard reaction compounds and lipids.[1,18] Frying temperature is an important parameter as it has a great influence on the formation of pyrazines in potato chips.[19,20] Brewer *et al*.[21] emphasize that odour characteristics of French fries reflect the odour characteristics of the frying oils, so that typical lipid oxidation products such as hexanal increase in the product when the same oil is used over a longer period.

Although potato flavour has received much attention, the number of papers about flavour compounds of French fries is limited. The doctoral thesis by Carlin [22] describes 429 volatiles extracted from French fries, and two papers have been published from this thesis: one focusing on alkyloxazoles [15] and the other on 3-(methylthio)alkanals.[23] There is however no information

about odour impact of the volatiles given. Wagner and Grosch [17] screened 48 compounds on their contribution to French fries flavour using aroma extract dilution analysis (AEDA) and gas chromatography-olfactometry of headspace samples (GCO-H). In a second paper [16] the authors evaluated the flavour profile of a model system with 21 potent flavour compounds dissolved in sunflower oil in comparison with the original extract. 2-Ethyl-3,5-dimethylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, 3-isobutyl-2-methoxypyrazine, 2,4-decadienal (*E,E*- and *E,Z*-), *trans*-4,5-epoxy-(*E*)-2-decenal, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, methylpropanal, 2- and 3-methylbutanal, and methanethiol were identified as character impact odorants.

Starch and lipids, both important constituents of French fries, are known to interact with flavour compounds.[24,25] Moreover, during consumption food is mixed and diluted with saliva by mastication, and starch will be degraded to some extent by amylase in saliva. The breakdown of the food matrix affects the food volatile composition,[26] but is often not taken into account when key flavour compounds are determined.

The aim of this study was to isolate and identify odour active compounds of French fries at mouth conditions. Mouth conditions will be created to mimic release of volatile compounds from the food to the nose epithelia, where odour is sensed, by taking into account the amount of product in relation to the mouth volume, the temperature, and by mixing the product with artificial saliva.

4.2 MATERIALS AND METHODS

Materials

French fries (10 × 10 mm, from variety Agria), obtained from Boots Frites BV (Purmerend, The Netherlands), were deep-fried in a Princess Classis household fryer (Princess Household Appliances, Middelharnis, The Netherlands) in partially hydrogenated vegetable frying oil (Remia, Den Dolder, The Netherlands, fatty acid composition: 9.7% C16:0, 5.9% C18:0, 72.3% C18:1, 11.5% C18:2, and 0.8 % C18:3) for 4 minutes at 180 °C.

Artificial saliva was prepared in demineralized water according to Van Ruth *et al*.[26] and consisted of K_2PO_4 (1.37 g/l), KCl (0.45 g/l), $CaCl_2 \cdot H_20$ (0.44 g/l), NaCl (0.88 g/l), $NaHCO_3$ (5.2 g/l), porcine stomach mucine (2.16 g/l, type II M2378, Sigma, Zwijndrecht, The Netherlands) and α-amylase from *A. oryzae* (10.5 g/l, type X-A, 500000 units, Sigma, Zwijndrecht, The Netherlands). NaN_3 (0.2 g/l) was used for preservation.

Isolation of volatile compounds

Volatiles were adsorbed on a glass tube (length 100 mm, 3.0 mm internal diameter) filled with 100 mg of Tenax TA (20/35 mesh, Alltech Nederland BV, Zwijndrecht, The Netherlands) using purge-and-trap. A sample of French fries was cut in pieces (<0.5 cm^3), 3.0 g was weighed and transferred into a glass flask (70 ml), and 4 ml of artificial saliva was added. The flask was placed in a water bath of 37 °C and a flow of purified nitrogen (50 ml/min) was passed through the sample for 30 min. The sample was mixed constantly by a magnetic stirrer. A cold trap with ethanol of –10 °C was used to prevent water vapour entering the Tenax tube.

Gas chromatographic analysis

Volatiles were desorbed onto the column using a thermal desorption unit (5 min at 245 °C) and cold trap (–120 °C/ 260 °C) device (Carlo Erba TDAS 5000, Interscience BV, Breda, The Netherlands). Compounds were separated on a 60 m × 0.25 mm × 0.25 μm Supelco MDN-5S capillary column (Sigma, Zwijndrecht, The Netherlands) in a Carlo Erba MEGA 5300 system (Interscience BV, Breda, The Netherlands). The oven temperature was kept at 40 °C for 4 min, and then increased to 270 °C at 4.0 °C/min with a final hold for 5 min. Helium was used as carrier gas at a constant pressure of 150 kPa and a FID detector was used at 300 °C. Retention indices of compounds were determined with a homologue series of alkanes (C5–C16) and relative areas of the compounds were calculated based on four replicates. Identification was performed with a Varian 3400 gas chromatograph (Varian, Bergen op Zoom, The Netherlands) equipped with a thermo desorption device (Chrompack TCT injector 16200, Chrompack, Middelburg, The Netherlands), coupled with a Finnigan MAT95 mass spectrometer (Thermo Electron, Bremen, Germany). The mass spectrometer was operated in the 70 eV EI ionisation mode and scanned from mass 24 to 320 with a cycle time of 0.65 s. Identification was made by

matching sample spectra against the Wiley/NIST 7th edition library and the Wageningen library, and by retention indices when available.[27,28]

Gas chromatography-olfactometry analysis (GC-O)

GC-O analysis was performed with a comparable system, column, and conditions as described in the previous paragraph. The effluent was however split 10:45:45 at the end of the column for FID detector and two sniffing ports respectively. Humidified air ran through stainless steel tubing to the sniffing port in order to prevent drying out of assessors' nasal membranes during the 40 min sniffing experiments.

Olfactometry data acquisition

Twelve assessors, nine females and three males aged 19 to 22, were selected for the olfactometry experiment from thirty volunteers. The selection procedure included a questionnaire and a test for odour sensitivity. The questionnaire was used to test their creativity by describing odours and odour differences between several products including French fries. Also questions about their availability and physical condition were included. The odour sensitivity test was carried out by putting a concentration series of 2-methylbutanal in paraffin (0.08, 0.13, 0.40, 2.0, and 10 µl/l) in ascending order. The concentration range was determined in preliminary experiments. Sixteen volunteers put the concentration either in the correct order or mixed up only two consecutive concentrations. Twelve of them were selected based on the results of the questionnaire.

The detection frequency method [29] was used to determine the importance of odour active compounds and a program to acquire sniffing data was written in Pascal. Assessors recorded the beginning and end of an odour by pressing a key on a laptop computer. The number of assessors detecting an odour simultaneously is used as a measure for the importance and from this data an aromagram can be constructed. Three training sessions were carried out with the same sample as in the final experiment to make the assessors familiar with the procedure. To generate flavour descriptors, assessors were asked to give a description at the end of each odour impression. From the list of descriptors twelve groups were created based on similarity and occurrence in a panel discussion. In the olfactometry experiment assessors were forced to choose the group best

describing the odour at the end of each odour impression. Blank Tenax TA tubes were used as dummy samples to determine the noise level of the panel. Retention index, mass spectrum, and odour description [30,31] were used to identify odour active compounds.

4.3 RESULTS AND DISCUSSION

The groups of odour descriptors resulting from the attribute generation and panel discussion are shown in Table 4.1.

Table 4.1 Descriptor groups used for olfactory analysis.

Group	Descriptor	Descriptors from attribute generation
1	French fries	French fries, potato chips, baked potato, frying fat, frying odour
2	baked flavour	popcorn, cookie, baked meat, baked fish, bread
3	potato, earthy	raw potato, cooked potato, earthy
4	nutty	nutty, peanut, almond, nougat, marzipan
5	chocolate	chocolate, cacao
6	sweet, flowery, fresh	sweet, flowery, mint, anise, apple, lemon, soap, pine, melon
7	butter, vanilla, caramel	butter, vanilla, caramel
8	grass, green	vegetable, grass, plant, cucumber, carrots
9	cheese, sweat	cheese, sweat
10	spicy	spicy, mushroom, wood, garlic, onion, leather, fungus
11	chemical, paint, glue	chemical, paint, glue, plastic
12	metal, burnt	metal, burnt

Because compounds often eluted closely after each other and assessors had to react quickly, we decided to create not more than twelve groups. For descriptors often mentioned (e.g. French fries, chocolate) a separate group was created, and from some similar descriptors a logical group name proceeded (e.g. nutty, green). For the remaining descriptors a general group name (e.g. spicy, baked flavour) was agreed on. A total of 122 compounds identified with GC-MS are listed in Table 4.2.

Table 4.2 Relative peak area and retention indices (RI) of volatile compounds identified in French fries, fried for 4 min at 180 °C.

Compounds by main origin	RI_{exp}	RI_{lit}	Relative peak area (%)
Lipid degradation			
ethanol [A, B, C, E]	< 500	503 [G]	3.1
2-propanol	514	524 [G]	4.1
methyl acetate	525	515 [G]	< 0.1
2,3-butanedione [A, B, C, E]	585	593 [G]	0.4
2-butanone [A, C, D, E]	589	597 [G]	0.3
2-methylfuran [B, C, D]	595	606 [G]	< 0.1
2-butanol [C, E]	601	591 [G]	< 0.1
methyl 2-propenoate	607		< 0.1
tetrahydrofuran	620	628 [G]	0.5
2-methyl-1-propanol [E]	624	619 [G]	< 0.1
acetic acid [A, B, C, E]	649	660 [G]	< 0.1
1-penten-3-ol [E]	682	683 [G]	< 0.1
2-pentanone	685	687 [G]	< 0.1
1-heptene	689	692 [G]	< 0.1
2-ethylfuran [B, C, D]	701	704 [G]	0.5
2-vinylfuran	721		< 0.1
2,5-dihydro-3,4-dimethylfuran [F]	732		< 0.1
2-methyl-2-butenal [C, D, E]	740	742 [H]	< 0.1
2-pentenal, (*E*)- [A, B, C, D]	753	754 [G]	< 0.1
methyl 2-butenoate, (*E*)-	761		< 0.1
1-pentanol [A, B, E]	765	771 [H]	< 0.1
toluene [B, C, D, E]	766	770 [G]	0.2
methyl 3-methylbutanoate	775	775 [G]	< 0.1
2-ethyl-5-methylfuran	775		< 0.1
3-hexanone [A, B, C, D, E]	783	787 [G]	< 0.1
2-methyl-3-hexanone	784	734 [G]	< 0.1
2-hexanone tentative [A, C, E]	787	789 [G]	< 0.1
2-propylfuran [C, E]	788	787 [G]	< 0.1
1-octene	790	792 [G]	< 0.1
cyclopentanone [C, E]	791		< 0.1
hexanal [A, B, C, D, E]	801	802 [H]	1.1
butanoic acid [C, E]	805	779 [G]	< 0.1
2-octene, (*E*)-	805	818 [G]	< 0.1

Table 4.2 Continued.

Compounds by main origin	RI_{exp}	RI_{lit}	Relative peak area (%)
Lipid degradation			
2-octene, (*Z*-) [B]	813	808 [G]	< 0.1
2-ethyl-2-butenal, (*E*)- [F]	815		< 0.1
2,5-furandione [F]	830		< 0.1
propylcyclopentane	833		< 0.1
2-hexenal, (*E*)- [A, B, C, D]	853	855 [H]	< 0.1
2-heptanone [A, B, C, E]	889	892 [H]	< 0.1
styrene [B, C, D]	893		0.1
heptanal [A, B, C, D, E]	902	902 [H]	0.4
acetylfuran [C, E]	910	912 [H]	< 0.1
propylcyclohexane [B, D]	935	939 [G]	< 0.1
butylcyclopentane	937	941 [G]	< 0.1
2-heptenal, (*E*)- [A, B, C, D]	959	956 [G]	0.3
5-methylfurfural [C]	962	964 [H]	< 0.1
1-heptanol [A, B, C, E]	971	967 [H]	< 0.1
phenol [E]	980	971 [G]	< 0.1
1-octen-3-ol [A, B, C, D, E]	981	979 [H]	< 0.1
hexanoic acid [B, C, E]	987	970 [G]	< 0.1
2-pentylfuran [A, B, C, D, E]	991	993 [G]	< 0.1
2,4-heptadienal, (*E,Z*)- [B, C]	998		< 0.1
octanal [A, B, C, D]	1005	1004 [G]	~ 0.2
2,4-heptadienal, (*E,E*)- [B, C, D, E]	1014	1009 [G]	< 0.1
5-ethyl-1-cyclopentene-1-carboxaldehyde	1035		< 0.1
benzyl alcohol [A, B, C, E]	1038		< 0.1
2-hydroxybenzaldehyde	1048	1045 [H]	< 0.1
2-octenal, (*E*)- [A, B, C, D, E]	1060	1060 [G]	0.2
acetophenone [D, E]	1071	1065 [H]	0.1
nonanal [B, C, D, E]	1107	1101 [H]	1.0
2-nonenal, (*E*)- [A, B, C, D, E]	1162	1162 [H]	< 0.1
benzoic acid [E]	1172		< 0.1
decanal [B, C, D, E]	1207	1202 [H]	< 0.1
2,4-nonadienal, (*E,E*)- [A, B, C, E]	1229	1212 [H]	< 0.1
2-decenal, (*E*)- [C, E]	1265	1264 [H]	< 0.1
2,4-decadienal, (*E,Z*)- [A, B, C, E]	1298	1293 [H]	< 0.1
2,4-decadienal, (*E,E*)- [A, B, C, E]	1323	1317 [H]	< 0.1

Table 4.2 Continued.

Compounds by main origin	RI_{exp}	RI_{lit}	Relative peak area (%)
Lipid degradation			
2-undecenal, (*E*)- [C]	1368	1366 [G]	< 0.1
1-undecanol	1374	1370 [H]	< 0.1
Total			14.6
Sugar degradation and/or Maillard reaction not involving sulfur amino acids			
2-methylpropanal [A, B, C, E]	554	552 [G]	20.3
3-methylbutanal [A, B, C, D, E]	658	654 [G]	29.3
2-methylbutanal [A, B, C, D, E]	669	662 [G]	31.4
2,3-pentanedione [B, C, E]	698	700 [H]	0.7
pyrazines	732		< 0.1
3-methyl-1-butanol [A, B, C]	734	737 [G]	< 0.1
1-methylpyrrole [C, D]	736	749 [G]	< 0.1
pyridine [A, B, C]	746	751 [G]	< 0.1
pyrrole	748	762 [G]	0.2
4,5-dimethyloxazole [F]	755		< 0.1
2,4,6-trimethyl-1,3,5-trioxane [C]	781	776 [G]	< 0.1
2-methylpropanoic acid [C, E]	797		0.8
dihydro-2-methyl-3(2H)-furanone [C, E]	807		< 0.1
1-ethylpyrrole	811	820 [G]	< 0.1
methylpyrazine [C, E]	825	826 [H]	0.7
furfural [A, B, C, D, E]	832	836 [H]	< 0.1
2-methylpyrrole [D]	843		< 0.1
3-methylbutanoic acid [C, E]	878	843 [G]	< 0.1
2-methylbutanoic acid [E]	888	838 [G]	0.2
2,5- and/or 2,6-dimethylpyrazine [C, E]	915	913 [H]	0.4
ethylpyrazine [C]	918	916 [H]	0.1
2,3-dimethylpyrazine [C, E]	921	920 [H]	0.3
vinylpyrazine [E]	934		< 0.1
benzaldehyde [A, B, C, D, E]	966	960 [H]	0.1
2-ethyl-6-methylpyrazine [C]	1000		0.2
2-ethyl-3-methylpyrazine [C]	1004	1003 [H]	~ 0.2
2-ethyl-5-methylpyrazine [C, E]	1006		~ 0.2
2-methyl-6-vinylpyrazine [E]	1020		< 0.1
isopropenylpyrazine	1021		< 0.1

Table 4.2 Continued.

Compounds by main origin	RI_{exp}	RI_{lit}	Relative peak area (%)
Sugar degradation and/or Maillard reaction not involving sulfur amino acids			
2-methyl-5-vinylpyrazine [C, E]	1025		< 0.1
1-methyl-2-pyrrolidinone	1043	1042 [G]	< 0.1
phenylacetaldehyde [A, B, C, D, E]	1048	1049 [G]	0.1
3-ethyl-2,5-dimethylpyrazine [C, E]	1079	1060 [G]	< 0.1
2,6-diethylpyrazine	1081		< 0.1
2,3-diethylpyrazine [C]	1082	1085 [H]	< 0.1
2-ethyl-3,5-dimethylpyrazine	1085		< 0.1
5-ethyl-2,3-dimethylpyrazine	1088		< 0.1
2,5-diethylpyrazine	1094		< 0.1
dimethylvinylpyrazine isomer [C, E, F]	1100		< 0.1
2,3-dihydroindole	1120		< 0.1
isobutylmethylpyrazine isomer [C, E]	1139	1137 [H]	< 0.1
2,3-diethyl-5-methylpyrazine [C, E]	1153		< 0.1
3,5-diethyl-2-methylpyrazine [C, E]	1157		< 0.1
methylpropenylpyrazine isomer [E]	1179		< 0.1
dimethylisobutylpyrazine isomer [C]	1201		< 0.1
isopentylmethylpyrazine isomer [E]	1254		< 0.1
isopentyldimethylpyrazine isomer [E]	1316		< 0.1
Total			85.4
Sulfur compounds			
dimethyl disulfide [B, C, D, E]	743	744 [G]	< 0.1
2-methylthiophene	770	779 [G]	< 0.1
3-methylthiophene	779	786 [G]	< 0.1
dimethyl trisulfide [B, C, D, E]	975	950 [G]	< 0.1
dimethyl tetrasulfide [B, C, E]	1241	1215 [G]	< 0.1
Total			< 0.1
Terpenes			
limonene [A, B, C, D, E]	1034	1031 [G]	< 0.1
Grand total			100

[A] found in raw potatoes [1,3]; [B] found in boiled potatoes [1,3-6]; [C] found in oven-baked potatoes [1,7-13]; [D] found in microwave baked potatoes [4,14]; [E] found in French fries [1,17,22]; [F] tentative identification; [G] according to Adams [28]; [H] according to Kondjoyan *et al*.[27]

Based on the relative areas approximately 85% of the aroma compounds originated from sugar degradation and/or Maillard reaction not involving sulfur amino acids and 15% were lipid-derived. Less than 0.1% consisted of a number of sulfur compounds and one terpene (limonene). Duckham *et al*.[7] compared volatiles from oven-baked potatoes of eleven cultivars, and found that the relative amount of lipid derived volatiles ranged from 22 to 69% among cultivars. For volatiles originating from sugar degradation and/or Maillard reaction not involving sulfur amino acids the range was from 25 to 77%. As the lipid content of raw potato is only 2–3 g/kg [7] and French fries are prepared in a large amount of oil, one might expect the amount of lipid-derived volatiles to be higher in French fries than in oven-baked potatoes. It seems however that the high heat transfer from the oil to the product is more favourable for sugar degradation and/or the Maillard reaction than for lipid degradation. Furthermore, melanoidines formed in the Maillard reaction are known to have an antioxidative effect.[32] This may have an effect on the amount of lipid-derived compounds, because the majority of these compounds is formed through oxidation. In this study fresh frying oil was used for all experiments. The composition of volatiles may however change as the frying oil gets older, because the odour characteristics of French fries reflect the odour characteristics of the oils in which they are fried.[21]

Many of the identified compounds have been described previously as volatiles from French fries or (processed) potato (see Table 4.2). The three main contributors of sugar degradation and/or Maillard reaction were 3-methylbutanal, 2-methylbutanal, and 2-methylpropanal, Strecker aldehydes of respectively isoleucine, leucine, and valine,[18] and they accounted for 81% of the total yield of volatiles. Other contributors were phenylacetaldehyde, the Strecker aldehyde of phenylalanine,[18] 2,3-pentanedione, and many heterocyclic, nitrogen containing compounds of which pyrazines were most abundant. A total of 26 pyrazines were found of which eleven have not been reported as volatiles from French fries, and six not from potato previously. Pyrazines are formed mainly from glutamine and asparagine, because these amino acids are present in potato in large quantities,[12,33] and pyrazines are considered to be key components of baked potato flavour.[13] Benzaldehyde was not put in the list of lipid-derived products as was done previously,[7,14] because it is formed from phenylacetaldehyde.[33] The formation of 2- and 3-methylbutanoic acid and 2-methylpropanoic acid can be explained by further oxidation of their corresponding aldehydes, the three main contributors. Lipid degradation resulted in the formation of several aldehydes, ketones, alcohols, hydrocarbons, acids, esters, and furans, of

which many are secondary oxidation products. The highest relative areas were obtained by ethanol, 2-propanol, nonanal, and hexanal. Nonanal is formed from oleic acid, which is the main fatty acid of the frying oil used, and hexanal is a typical oxidation product of linoleic acid.[18,21] Ethanol and 2-propanol are probably formed after several degradation steps, induced by the high frying temperature. The three sulfides and two thiophenes that were found in this study were formed from sulfur containing amino acids. As these sulphides are formed in the Maillard reaction they have been found in boiled, baked, and fried potato, but not in raw potato. 2- and 3-Methylthiophene were suggested to be formed from the interaction between fatty aldehydes and cysteine.[34] 2-Pentanone and 1-methyl-2-pyrrolidinone have not been found in potato, but they have been reported as volatiles from cured ham.[35] Methional and methanethiol, both appointed as potent odorants of French fries flavour,[17] were not detected.

In Figure 4.1 the chromatogram from the FID-detector and the aromagram resulting from the olfactometry experiments is shown, and identification of the 41 peaks is explained in Table 4.3. Not all aromagram peaks could be identified conclusively, because sometimes compounds having similar odours eluted closely after each other. Compounds with the highest detection frequency contribute most to French fries flavour. In this way 2-methylbutanal and/or 3-methylbutanal, hexanal, 2,3-dimethylpyrazine, 2-methylpropanal, 2,3-butanedione, pyridine, heptanal, 2,5-dimethylpyrazine and/or 2,6-dimethylpyrazine and/or ethylpyrazine, dimethyl trisulfide, octanal, phenylacetaldehyde, 2,5-diethylpyrazine, (*E*)-2-nonenal, 2-methylbutanoic acid and/or 3-methylbutanoic acid, (*E,Z*)-2,4-heptadienal, (*E*)-2-octenal, 5-ethyl-2,3-dimethylpyrazine and/or 2-ethyl-3,5-dimethylpyrazine, nonanal, and tentatively 2-methylpyrrole were found to be the most important odour active compounds of French fries.

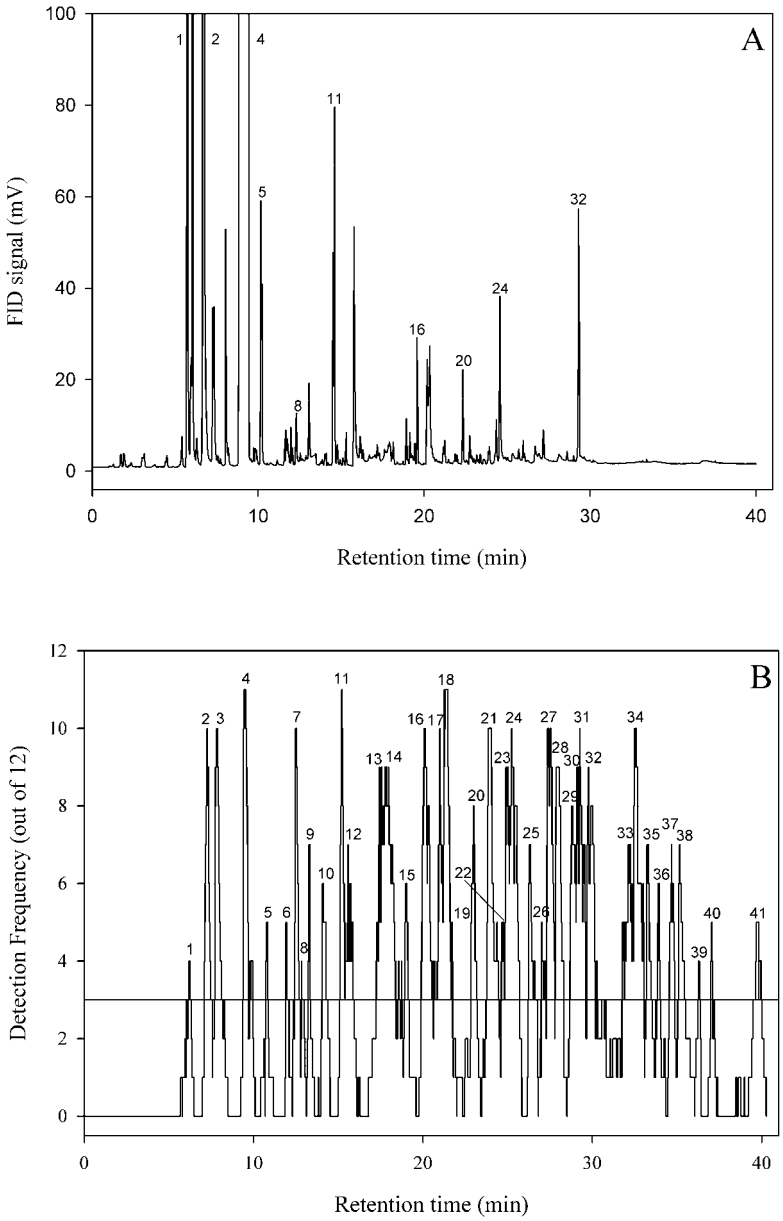

Figure 4.1 Aromagram of dynamic headspace samples. FID response (A) and detection frequency of assessors at sniffing port (B). Horizontal line in (B) represents noise level.

Table 4.3 Detection frequency and odour description of odour active compounds from French fries.

Peak no.	Retention time on GC-O	RI [A]	Detection frequency	Odour group [B]	Compound
1	6.19	<500	4	5, 6, 11	ethanol
2	7.25	550	10	7, 5, 9, 11	2-methylpropanal
3	7.83	585	10	7	2,3-butanedione
4	9.44	660	11	11, 9, 5, 7	3-methylbutanal and 2-methylbutanal
5	10.76	700	5	7	2,3-pentaandion
6	11.92	730	5	6	2,5-dihydro-3,4-dimethylfuran (tentative)
7	12.51	745	10	11	pyridine
8	12.84	755	4	11, 6, 1	pyrrole
9	13.26	760	7	6	methyl 2-butenoate, (*E*)-
10	14.07	775	6	11, 9	2-methylpropanoic acid
11	15.21	800	11	6, 8	hexanal
12	15.57	810	7	1, 10	1-ethylpyrrole (tentative)
13	17.42	845	9	9, 3	2-methylpyrrole (tentative)
14	17.75	855	9	11, 9	3-methylbutanoic acid and/or 2-methylbutanoic acid
15	18.97	880	6	3	unknown
16	20.07	900	10	8, 3, 6	heptanal
17	21.00	920	10	3, 1, 12	2,5-dimethylpyrazine, 2,6-dimethylpyrazine and/or ethylpyrazine
18	21.30	925	11	2, 4	2,3-dimethylpyrazine
19	21.70	935	5	1, 2	vinylpyrazine
20	22.97	960	8	3	2-heptenal, (*E*)-
21	23.87	980	10	9, 10, 2, 12	dimethyl trisulfide
22	24.67	995	5	6	2-pentylfuran
23	24.90	1000	9	6, 1	2,4-heptadienal, (*E,Z*)-
24	25.23	1005	10	6, 1	octanal
25	26.29	1025	7	2, 12, 4	2-methyl-5-vinylpyrazine
26	27.01	1045	5	3, 11	1-methyl-2-pyrrolidinone (tentative)
27	27.36	1050	10	3, 12, 6, 8	phenylacetaldehyde
28	27.87	1060	9	8, 11, 10, 7	2-octenal, (*E*)-
29	28.67	1080	8	3, 11, 2, 10	3-ethyl-2,5-dimethylpyrazine, 2,3-diethylpyrazine and/or 2,6-diethylpyrazine
30	29.09	1090	9	6, 2, 10	5-ethyl-2,3-dimethylpyrazine and/or 2-ethyl-3,5-dimethylpyrazine
31	29.27	1095	10	6, 3, 12, 11	2,5-diethylpyrazine

Table 4.3 Continued

Peak no.	Retention time on GC-O	RI [A]	Detection frequency	Odour group [B]	Compound
32	29.76	1105	9	1, 8	nonanal
33	32.11	1155	7	3, 6, 9	3,5-diethyl-2-methylpyrazine and/or 2,3-diethyl-5-methylpyrazine
34	32.48	1170	10	8	2-nonenal, (*E*)-
35	33.22	1180	7	2, 4	pyrazine, methylpropenyl isomer
36	33.89	1200	6	8, 6, 3, 12	pyrazine, dimethylisobutyl isomer
37	34.67	1215	7	8	decanal
38	35.16	1230	7	2, 1, 4, 11	2,4-nonadienal, (*E,E*)-
39	36.26	1255	4	8, 2, 3	pyrazine, isopentylmethyl isomer
40	37.02	1275	5	6, 7, 2, 12	2-decenal, (*E*)-
41	39.68	1330	5	1	2,4-decadienal, (*E,E*)-

[A] Retention index estimated by 30–40 s delay between FID-signal and flavour perception.

[B] See Table 4.1.

2-Methylpropanal, 3-methylbutanal and 2-methylbutanal were perceived by almost all assessors. It was difficult for the assessors to notice a difference between 3- and 2-methylbutanal, resulting in a large peak with a small shoulder. The odour is usually referred to as chocolate or malty, but some assessors described it as sweaty, which corresponds to what Berdagué *et al*.[35] found. Pyrazines were responsible for eleven peaks in the aromagram and resulted in the dominant fried potato note. C2- and C4-substituted pyrazines eluted closely after each other making it difficult to identify the one responsible for peak 13 and peak 29–31 respectively. 2,3-Butanedione and to a lesser extent 2,3-pentanedione contributed to the caramel or buttery note. Fatty aldehydes, of which hexanal, heptanal, octanal, (*E*)-2-nonenal, and nonanal were the most important representatives, were perceived as green odours. These compounds are however known to cause a rancid off-flavour.[18,21] We confirm that alkadienals, such as (*E,E*)-2,4-decadienal, (*E,E*)-2,4-nonadienal, and (*E,Z*)-2,4-heptadienal, contribute to the deep-fried note.[17] Dimethyl trisulfide, phenylacetaldehyde, and possibly 2-methylpyrrole cause a spicy note. Based on retention index and mass spectrum peak 13 could be 2-methylpyrrole, however no information about the odour description could be found in literature. Although the chemical odour from pyridine, and sweaty odour from 3-methylbutanoic acid and 2-methylbutanoic acid were clearly noticed by the panel,

they do not seem to give a distinct note, but may influence the perceived aroma as a whole. 2-Methylbutanoic acid and 3-methylbutanoic acid had a very broad peak and that is the reason why the retention index is higher than the literature value in Table 4.2. As these compounds were dominating the mass spectra around peak 15, it was not possible to identify the compound responsible for the potato or earthy odour.

Although the potato variety used was the same, the results were different from what Wagner and Grosch [17] found. They did not find chemical or sweaty odours such as pyridine and 3-methylbutanoic acid, and that we did not find methional and methanethiol. This can be explained by using different methods for sample preparation and extraction. Other factors such as storage conditions of the potatoes,[13] the type of frying oil,[21] and the frying temperature [20,33] may play a role as well.

4.4 CONCLUSION

Isolation of French fries flavour by purge-and-trap using conditions during consumption yielded 122 identified volatiles of which 85% of the relative area originated from sugar degradation and/or Maillard reaction. 2-Methylpropanal, 2-methylbutanal, 3-methylbutanal, and 26 pyrazines were the main representatives. 15% of the volatiles were lipid-derived and ethanol, 2-propanol, hexanal, and nonanal showed the highest relative areas of this group. About 50 odour active compounds were, due to co-elution, responsible for 41 odours perceived by the panel. The compounds with the highest detection frequencies caused a strong malty note and fried potato note, combined with caramel/ buttery, green, spicy, and deep-fried notes. Also chemical and sweaty odours were observed.

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Chapter 5

Real time flavour release from French fries using MS-Nose

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ABSTRACT

Flavour release from French fries was measured with MS-Nose using both assessors (*in vivo*) and a mouth model system (*in vitro*). Several volatiles measured with MS-Nose could be identified with MS-MS. The effect of frying time, salt addition, and an alternative process using superheated steam was determined on I_{max} (maximum intensity of compounds) and on t_{max} (time of maximum intensity). *In vitro* a "chewing" frequency of 0.60 Hz caused an increased t_{max} for low molecular compounds. Above 0.93 Hz further increasing the frequency did not affect t_{max}. Trends observed with *in vivo* experiments could be verified with *in vitro* experiments. I_{max} correlated well with frying time. Addition of salt resulted in a decreased t_{max} suggesting a salting-out effect. The alternative process caused a layer of oil on the surface and this resulted in a higher t_{max}, but no effect on I_{max} was found. This phenomenon may be critical for the sensory quality, and would not have been observed with static volatile measurements, demonstrating the value of flavour release measurements.

5.1 INTRODUCTION

Since the introduction of fast food restaurants, French fries have become a popular food all over the world. Apart from texture, flavour is one of the most important quality aspects. The flavour of potato has received much attention by researchers, and more than 500 volatiles have been identified.[1] The flavour composition changes considerably by different ways of processing.[2] Enzymatic degradation of unsaturated fatty acids by lipoxygenase is important for raw potato flavour. Enzymes are inactivated during cooking, and methional, formed in the Maillard reaction, is a key compound of cooked potato flavour.[3] In oven-baked potatoes, where higher temperatures are applied, an increased number of Maillard reaction products was found.[4] Microwave-baked potatoes have a composition of volatile compounds in between cooked and oven-baked potatoes.[5] The amount of heterocyclic compounds from the Maillard reaction is the highest in deep-fried potato products due to the high heat transition.[6] Additionally, frying in oil yields flavour compounds derived from lipid degradation and from interactions between lipids and Maillard reaction products.[7]

Several authors studied the flavour of French fries. A dissertation on this subject [8] focused on the identification of volatiles, but no information on the odour impact was given. Wagner and Grosch [9,10] identified 48 odorants of French fries by application of both Aroma Extraction Dilution Analysis and GC-Olfactometry. Van Loon *et al*.[11] used purge and trap to extract volatile compounds mimicking mouth conditions. GC-FID, GC-MS, and GC-Olfactometry were used to identify odour active compounds. Based on relative peak areas, 85% was found to originate from sugar degradation and/or Maillard reaction, while 15% was lipid-derived. With GC-Olfactometry 50 odour active compounds were found, of which 2-methylbutanal and/or 3-methylbutanal, hexanal, 2,3-dimethylpyrazine, 2-methylpropanal, 2,3-butanedione, pyridine, heptanal, 2,5-dimethylpyrazine and/or 2,6-dimethylpyrazine and/or ethylpyrazine, dimethyl trisulfide, octanal, phenylacetaldehyde, 2,5-diethylpyrazine, and (*E*)-2-nonenal were found to be the most important compounds.

With the introduction of new mass spectrometric methods it is possible to sample volatile compounds in the nose space of assessors during eating.[12,13] MS-Nose, based on atmospheric

pressure chemical ionisation, has been used both on model systems [14-16] and on food systems.[17,18] The method proved to be suitable to measure flavour release in real time, and good correlations with sensory perception were found. Mouth model systems have been designed to mimic eating dynamics *in vitro*.[19-26] In general, the food is blended and volatiles are trapped on an absorbent. Although these devices usually do not include inhaling and swallowing, they have the advantage to cause less variation than assessors.[19]

Knowledge of flavour release could give information about the sensory perception during consumption of French fries, but this has not been studied until now. Therefore, the aim of this study was to follow the *in vivo* and *in vitro* flavour release from French fries in real time. The effect of frying time and salt addition on flavour release were determined. Recently, a new energy efficient process for the production of French fries was proposed (Chapter 2). The effect of this process on flavour release was studied as well.

5.2 MATERIALS AND METHODS

Materials

For all experiments potato strips with a cutting size of 10 × 10 mm were used, produced from potatoes of the variety Agria. Conventional par-fried, frozen French fries were kindly provided by Boots Frites BV (Purmerend, The Netherlands). French fries were also prepared by an alternative, energy efficient process, in which superheated steam was used (Chapter 2). After conventional blanching potato strips were treated with superheated steam for 25 min at 0.47 bar, with a steam temperature of 110 °C, and a steam flow of 115 kg/h. After finish-frying in oil the French fries of the alternative process had a reduced oil content compared to the conventional product (–30%).

Partially hydrogenated vegetable oil (Remia, Den Dolder, The Netherlands) was used for finish-frying. French fries of about 6 cm length were selected and fried individually in a Princess Classic household fryer (Princess Household Appliances, Middelharnis, The Netherlands) at 180 °C.

Artificial saliva was prepared in demineralized water according to Van Ruth *et al*.[27] and consisted of K_2PO_4 (1.37 g/l), KCl (0.45 g/l), $CaCl_2 \cdot H_20$ (0.44 g/l), NaCl (0.88 g/l), $NaHCO_3$ (5.2 g/l), porcine stomach mucine (2.16 g/l, type II M2378, Sigma, Steinheim, Germany) and α-amylase from *A. oryzae* (10.5 g/l, type X-A, 500000 units, Sigma, Steinheim, Germany). NaN_3 (2 ml of 10% solution) was used for preservation.

General set-up

After finish-frying, flavour release from French fries was measured by MS-Nose both in exhaled breath of assessors (*in vivo*) and in a mouth model system (*in vitro*). The maximum intensity (I_{max}) and time of maximum intensity (t_{max}) of released flavour compounds were determined to evaluate the effect of frying time (2, 4, 6, and 8 min), the effect of salt addition (0.1 g per French fry), and the effect of the alternative process for the production of French fries. The amount of salt was based on preliminary experiments. All salt particles stuck to the French fries and a nice, salty taste was obtained.

Identification of released flavour compounds

Concentrations of flavour compounds were measured on-line by an atmospheric pressure chemical ionisation (APCI) gas phase analyser attached to a VG Quattro II mass spectrometer (Micromass UK Ltd., Manchester, UK). Compounds were ionised by a 3.0 kV discharge (source and probe temperatures were 80 °C), and scanned for *m/z* 40–250. *M/z* values of observed compounds were selected and fragmented with argon for identification. In further experiments compounds were monitored in selected ion mode with 0.08 s dwell time on each ion.

In vivo flavour release in exhaled breath

Flavour release was measured in exhaled breath of three experienced assessors in triplicate. Assessors breathed in and out through a tube in the nose (0.53 mm internal diameter, heated to 100 °C), from which continuously 80 ml/min of air was sampled directly into the MS-Nose. A strict protocol was followed during the experiments. After putting one French fry in the mouth, assessors immediately started chewing at a rate of about one chewing movement per second. The sample was swallowed after 30 s and chewing movements were continued until 60 seconds.

Between samples the mouth was rinsed with water. Blank experiments were recorded with water following the same protocol. Acetone, present in human breath, was measured at *m/z* 58.8 (19 V) as indicator for the breathing pattern.

In vitro flavour release in the mouth model system

Dynamic headspace measurements were carried out in triplicate with a mouth model system developed by Van Ruth *et al*.[23] The mouth model consists of a double wall glass housing with an inner volume comparable to the human mouth in which a plunger moves up and down and rotates simultaneously to simulate chewing. Water of 37 °C is pumped through the double wall. One French fry was put in the mouth model system and 3.5 ml of artificial saliva was added. The volume of artificial saliva was determined in a preliminary experiment by having the panellists chew a French fry for 30 s and measure the weight gain. Five "chewing" frequencies of the mouth model system (0.60, 0.93, 1.27, 1.60, and 1.93 Hz) were tested for optimisation. An airflow of 80 ml/min was sampled directly into the MS-Nose. Flavour release was monitored for 5 min after "chewing" started.

Calibration of flavour release measurements

MS-Nose measurements were calibrated according to the method of Weel *et al*.[28] in order to quantify the identified compounds. In short, a known amount of each flavour compound (1 ml of a 0.05 mg/l solution in artificial saliva) was put in the mouth model system without the plunger. The solution was continuously stirred and sampled into the MS-Nose. The measurement was recorded until the signal had returned to the baseline. The area under the curve corresponds to the total amount of aroma present in the solution. The concentration of the flavour compound in the air C_g (µg/l) was calculated from the release signal in arbitrary units (au) according to equation 5.1.

$$C_g = \frac{M}{A \times F} \times signal \qquad (5.1)$$

M is the amount of flavour compound present in the solution (µg), A is the area under the curve (au × min), and F is the flow of sampled air (l/min).

Statistical analysis

SPSS 10.0.7 was used for statistical evaluation of the data. Linear regression was used for the effect of frying time and "chewing" frequency. MANOVA with General Linear Model followed by a post hoc test according to Tukey was used to calculate the effect of salt addition and the alternative process. A significance level of $\alpha \leq 0.05$ was used throughout the study.

5.3 RESULTS AND DISCUSSION

Identification of detected compounds

Release of in total eleven compounds could be observed *in vitro*, of which five were also found *in vivo* (Table 5.1).

Table 5.1. Compounds observed with MS-Nose and identified by MS-MS.

M/z	Cone (V)	Compound	Observed	References [A]
69	20	n.i. [B] (fragmentation pattern: *m/z* 69: 100%, *m/z* 41: 65%, *m/z* 39: 5%, *m/z* 29: 9%)	*in vivo, in vitro*	-
73	20	methylpropanal	*in vivo, in vitro*	(*1, 4, 9*)
75	23	n.i. (fragmentation pattern: *m/z* 75: 100%, *m/z* 57: 6%, *m/z* 43: 23%, *m/z* 29: 8%, *m/z* 15: 5%)	*in vitro*	-
87	16	2- and/or 3-methylbutanal	*in vivo, in vitro*	(*1, 4, 5, 9*)
91	10	n.i. (fragmentation pattern: *m/z* 91: 100%, *m/z* 73: 111%, *m/z* 58: 9%, *m/z* 55: 44%, *m/z* 45: 22%, *m/z* 43: 10%, *m/z* 31: 14%, *m/z* 29: 12%)	*in vitro*	-
95	20	methylpyrazine	*in vivo, in vitro*	(*1, 4, 5*)
109	30	C2-pyrazine (dimethyl-, ethyl-)	*in vivo, in vitro*	(*1, 4, 5*)
113	20	2-heptenal	*in vitro*	(*1, 3, 5*)
123	37	C3-pyrazine (ethylmethyl-)	*in vitro*	(*1, 4, 5*)
137	37	C4-pyrazine (ethyldimethyl-, diethyl-)	*in vitro*	(*1, 5, 9*)
153	21	2,4-decadienal	*in vitro*	(*1, 3, 5, 9*)

[A] References reporting compounds previously found in potato or potato products

[B] Not identified

This difference was caused by the different way of sampling, and was reported by Deibler *et al*.[19] as well. Identification of compounds detected during flavour release is a difficult task, because it puts high demands on MS equipment. The technique has to be fast and sensitive, and it has to be capable of handling air and water, and simultaneous detection of compounds. Techniques involving ionisation based on proton transfer (APCI, PTR) followed by MS can overcome these problems.[29] Fragmentation of the compounds is generally necessary for conclusive identification. However, these soft ionisation techniques mainly produce single ions from compounds. In the present study selected ions were fragmented with argon and analysed in a second MS. This elegant, direct method made unequivocal identification of several compounds possible. In accordance with literature,[4] the observed compounds originated from either the Maillard reaction or lipid degradation. The highest signal was obtained for 2- and/or 3-methylbutanal and this corresponded to previous findings.[11] Methylpropanal, 3-methylbutanal, and 2-methylbutanal are Strecker aldehydes from valine, leucine, and isoleucine respectively [7] and pyrazines are known Maillard reaction products as well.[6,30] (*E*)-2-heptenal and (*E,E*)-2,4-decadienal are formed from autoxidation of linoleic acid.[31,32] *M/z*-value 69, 75, and 91 could not be identified. As the fragmentation pattern of *m/z* 87 showed a high peak of *m/z* 69, it is possible that *m/z* 69 is a fragment of 2- and/or 3-methylbutanal. Identified compounds are expressed as their concentration in air, whereas the release of the unknown *m/z*-values 69, 75, and 91 is expressed in arbitrary units. For the pyrazines it was not possible to make a conclusive identification. *M/z* 137, for example, could be 2,3-diethylpyrazine, 2-ethyl-3,5-dimethylpyrazine or another isomer. A mixture of two or more isomers is possible as well. Therefore, an estimation of the concentration in air was made in the calibration experiments using pyrazines with the same *m/z*-value. Based on previous results [11] 2-methylpyrazine was used for *m/z* 95, 2,5-dimethylpyrazine for *m/z* 109, 3-ethyl-2-methylpyrazine for *m/z* 123, and the average value of 2,3-diethylpyrazine and 2-ethyl-3,5-dimethylpyrazine was used for *m/z* 137.

Effect of "chewing" frequency on t_{max} for in vitro experiments

To optimise the procedure for *in vitro* measurements, t_{max} was determined for a number of "chewing" frequencies (Figure 5.1).

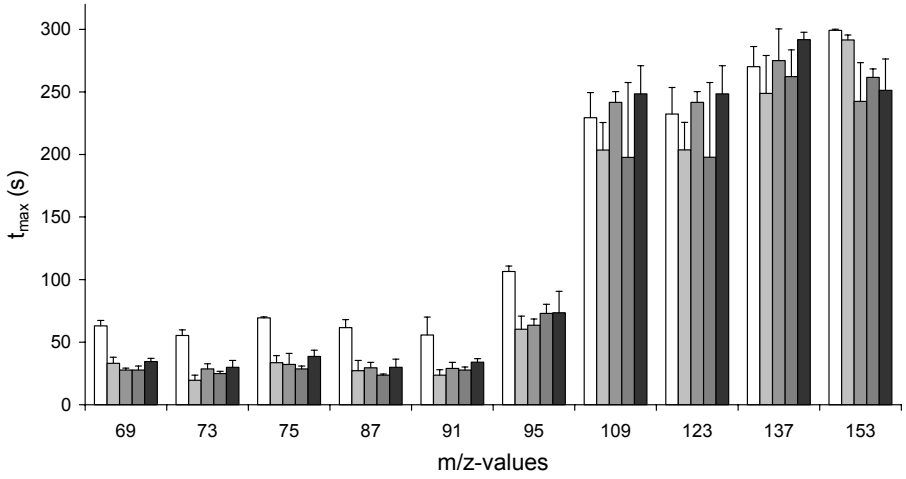

Figure 5.1. t_{max} *in vitro* of compounds released from French fries at a "chewing" frequency of 0.60 (white), 0.93 (light-grey), 1.26 (medium-grey), 1.60 (dark-grey), and 1.93 Hz (black). Error bars represent the standard error.

Lower molecular compounds (*m/z* 69 to 95) reached t_{max} at about 60 s, whereas higher molecular compounds (*m/z* 109 to 153) only reached t_{max} after 3–5 min. With MANOVA it was shown that the lowest frequency (0.60 Hz) caused the lower molecular compounds to release significantly slower than the other frequencies. From 0.93 Hz t_{max} did not further decrease upon a higher frequency. No significant effect of "chewing" frequency on the t_{max} of *m/z* values 109, 123, 137, and 153 was found. In other words, the t_{max} of fast releasing compounds was affected by a low "chewing" frequency, whereas slow releasing compounds were not additionally slowed down. For *in vitro* experiments a "chewing" frequency of 1.60 Hz was chosen, because it did not influence the release of any of the selected compounds. Furthermore, it was considered as a normal chewing rate for humans.

Effect of frying time on I_{max} and t_{max}

For all compounds I_{max} increased linearly with frying time (Figure 5.2).

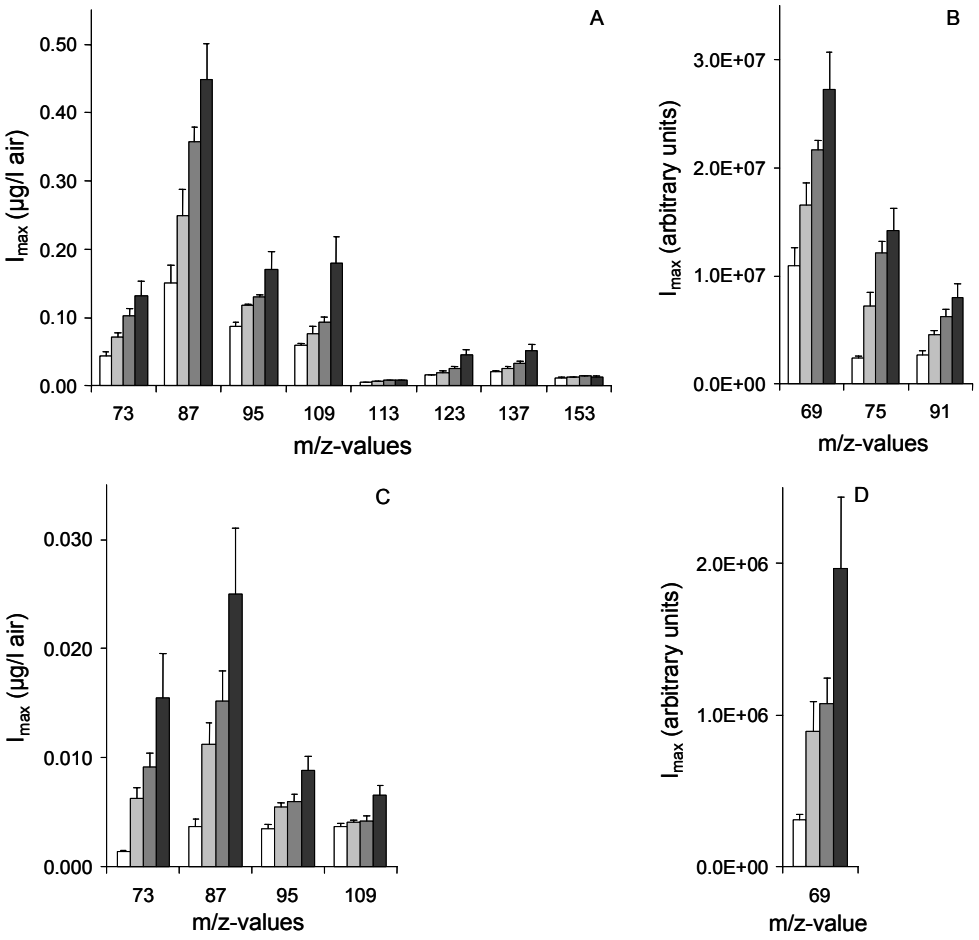

Figure 5.2. I_{max} *in vitro* (A and B) and *in vivo* (C and D) of compounds released from French fries at 2 min (white), 4 min (light-grey), 6 min (dark-grey), and 8 min (black) of frying at 180 °C. A and C show the identified compounds, B and D show the unknown compounds. Error bars represent the standard error.

As frying proceeds, surface moisture evaporates, and the temperature gradually increases. A high temperature and reduced moisture content are favourable conditions for the Maillard reaction.[33] This is in accordance with the observation that the colour became darker as the frying time increased. *M/z* 113 (2-heptenal) and 153 (2,4-decadienal) increased to a lesser extent than the other compounds, because these compounds originated from lipid oxidation. The highest I_{max} value was reached for *m/z* 87 (2- and/or 3-methylbutanal). Martin and Ames [6] reported high concentrations of 2- and 3-methylbutanal in fried potato model systems compared to pyrazines. I_{max} was higher *in vitro* than *in vivo*, because, as already mentioned, the amount of sample that entered the MS-Nose from the mouth model system was higher. The correlation coefficient of linear regression was higher *in vitro* (0.60–0.85) than *in vivo* (0.25–0.55). This may be explained by differences among assessors such as geometry of the mouth, saliva production, and chewing behaviour.

No significant effect of frying time on t_{max} was found (Figure 5.3). There was, however, a distinct difference between *in vivo* and *in vitro* experiments. For *in vivo* experiments all compounds had a t_{max} of less than 10 s, whereas *in vitro* the fastest releasing compounds had a t_{max} of about 60 s. Apparently, the plunger in the mouth model system was less effective in releasing flavour compounds than mastication in the human mouth. Also, compounds had to cover a longer distance in the mouth model system to enter the MS-Nose. The difference in volatility may have caused higher molecular compounds such as pyrazines to release slower than lower molecular aldehydes.

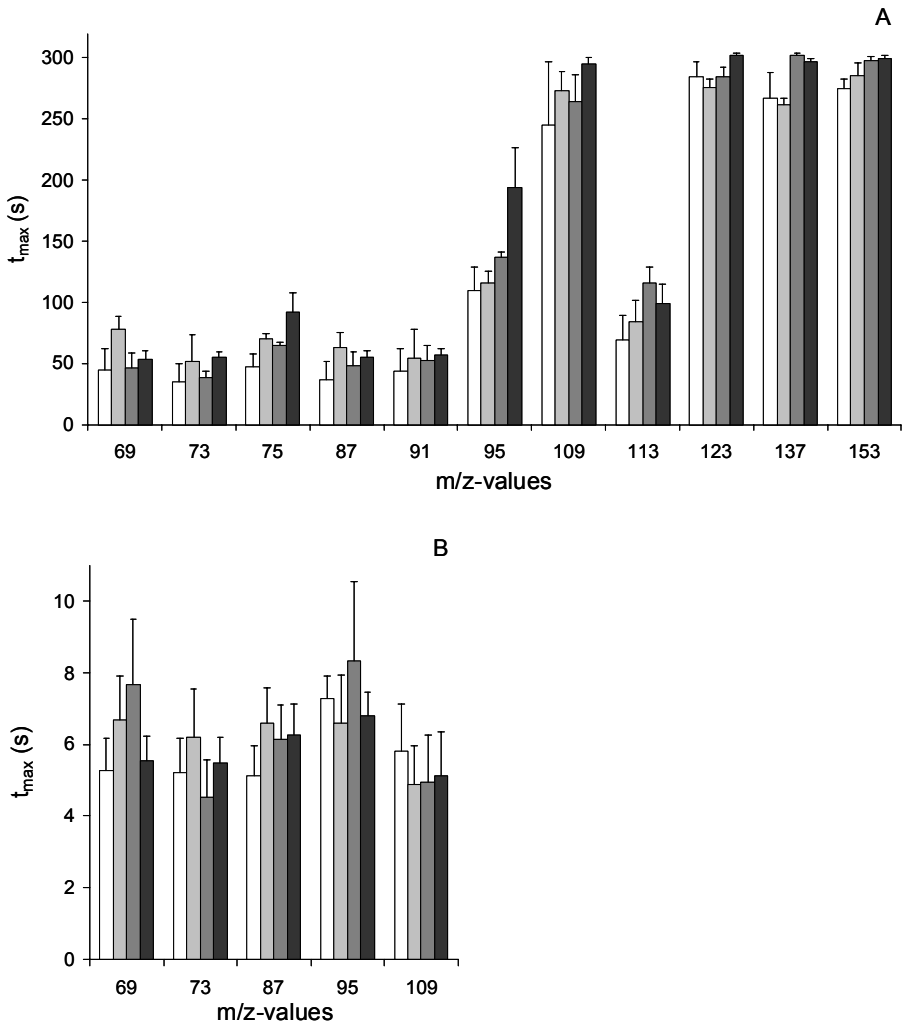

Figure 5.3. t_{max} *in vitro* (A) and *in vivo* (B) of compounds released from French fries at 2 min (white), 4 min (light-grey), 6 min (dark-grey), and 8 min (black) of frying at 180 °C. Error bars represent the standard error.

Effect of salt addition on I_{max} and t_{max}

A trend was observed for both *in vitro* and *in vivo* experiments that I_{max} decreases when salt was added (Figure 5.4), but the effect was not significant.

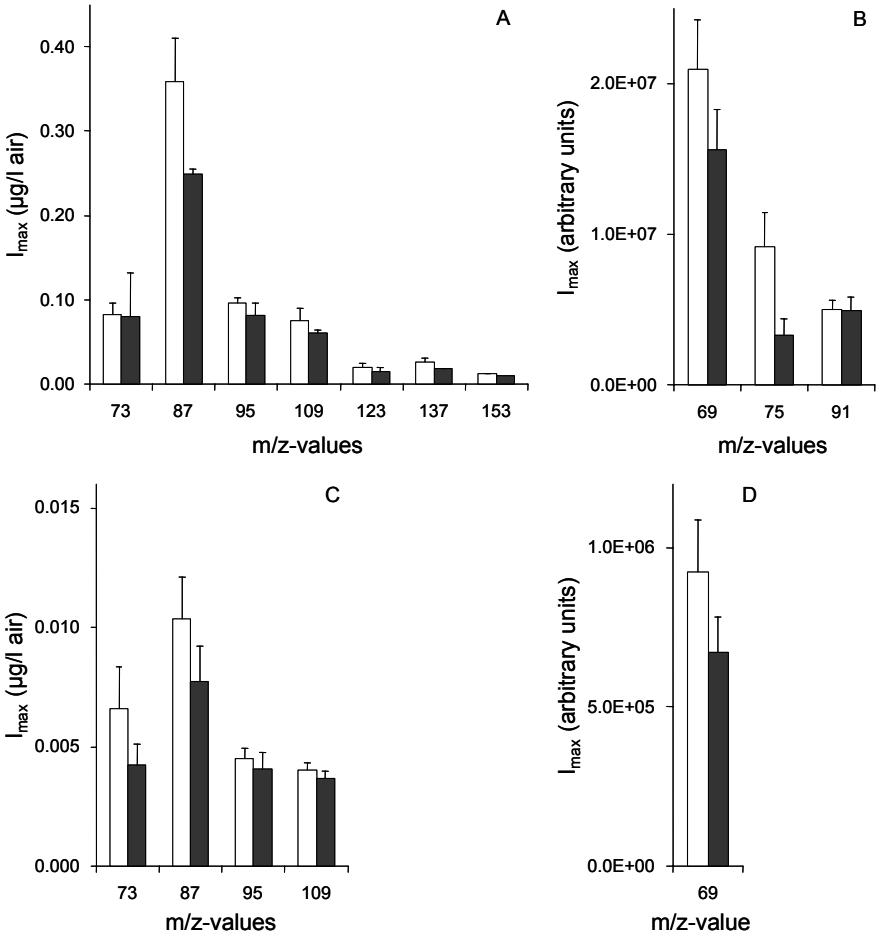

Figure 5.4. I_{max} *in vitro* (A and B) and *in vivo* (C and D) of compounds released from French fries without salt addition (white) and with salt addition (black). A and C show the identified compounds, B and D show the unknown compounds. Error bars represent the standard error.

Salt and increased saliva production (*in vivo*) may have had an effect on the partition coefficient of some compounds. The effect of salt addition on t_{max} is shown in Figure 5.5.

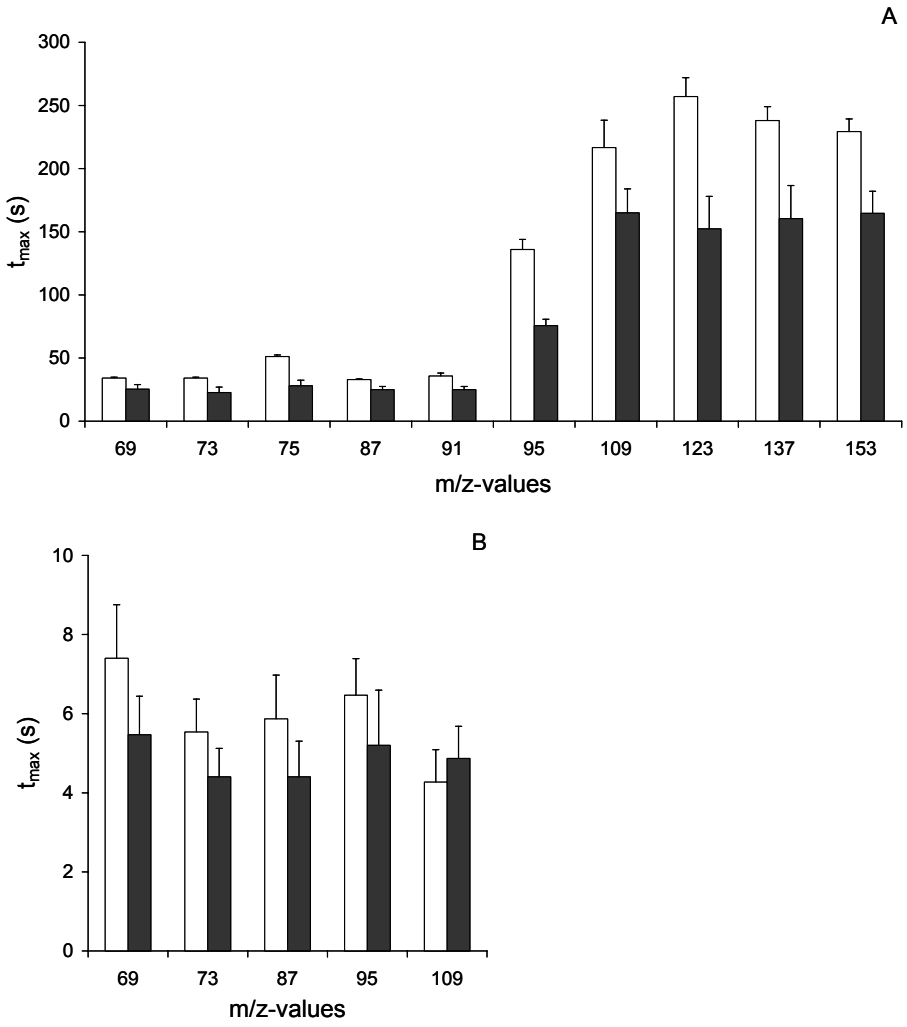

Figure 5.5. t_{max} *in vitro* (A) and *in vivo* (B) of compounds released from French fries without salt addition (white) and with salt addition (black). Error bars represent the standard error.

There was a significant decrease of t_{max} by addition of salt *in vitro*. The effect on t_{max} was not significant for *in vivo* experiments, but showed the same trend. The faster release of compounds after salt addition may be explained by a salting-out effect, causing the concentration of compounds in the air phase to increase.[27,34]

Effect of the alternative process on I_{max} and t_{max}

The effect of the alternative process for the production of French fries using superheated steam on I_{max} and t_{max} is shown in Figure 5.6 and 5.7 respectively. The variation of experiments with assessors was higher than that of experiments with the mouth model system, and this is in accordance with the effect of frying time and the effect of salt addition. There was no significant difference in I_{max} between French fries produced with the alternative and the conventional process. However, the alternative process resulted in a higher t_{max} of released compounds than the conventional process. This may have a strong impact on the sensory quality, and would not have been observed with static volatile measurements alone, demonstrating the value of flavour release measurements. The French fries produced with the alternative process had a reduced oil content of about 30%. As lipids are known to retain nonpolar flavour compounds,[22,27] the t_{max} of the compounds was expected to be higher for the conventional process. However, superheated steam, which was used in the alternative process, caused a skin on the surface of the French fries. The skin hindered evaporation of water during finish-frying in oil, and absorption of oil thereafter (Chapter 2). Although the oil content was lower, the oil was concentrated in a layer on the surface and this has may have caused the release of flavour compounds to slow down.

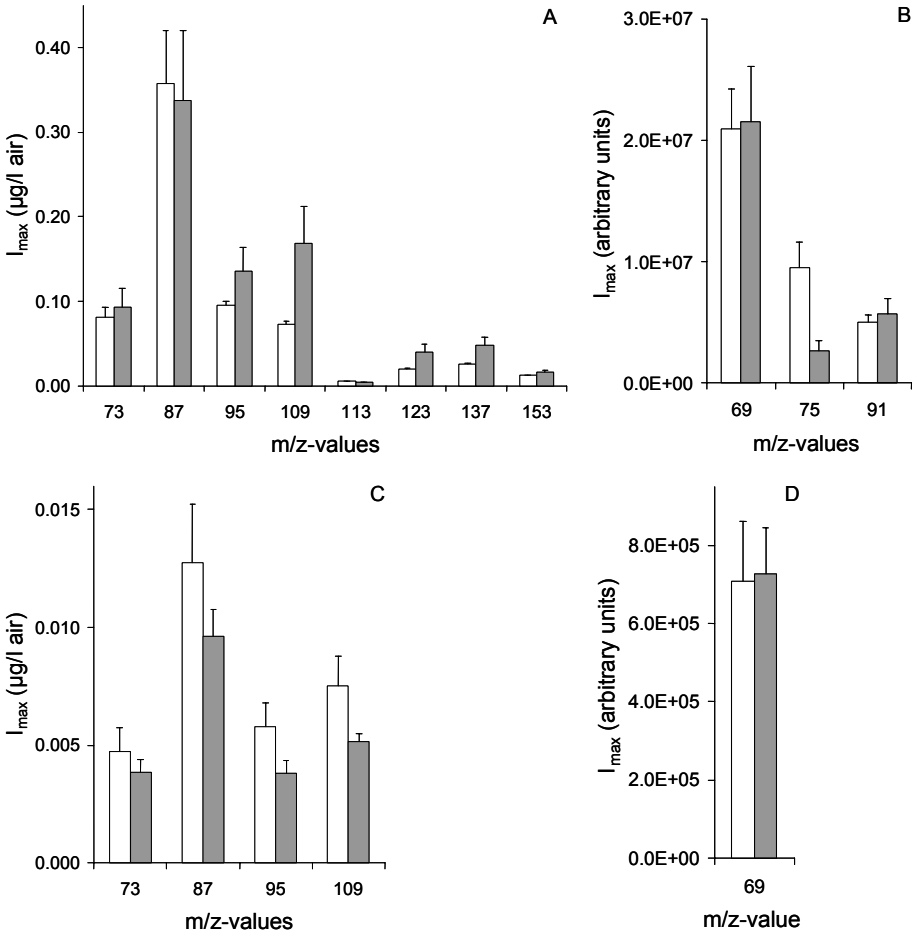

Figure 5.6. I_{max} *in vitro* (A and B) and *in vivo* (C and D) of compounds released from French fries produced according to conventional process (white) and the alternative process (grey). A and C show the identified compounds, B and D show the unknown compounds. Error bars represent the standard error.

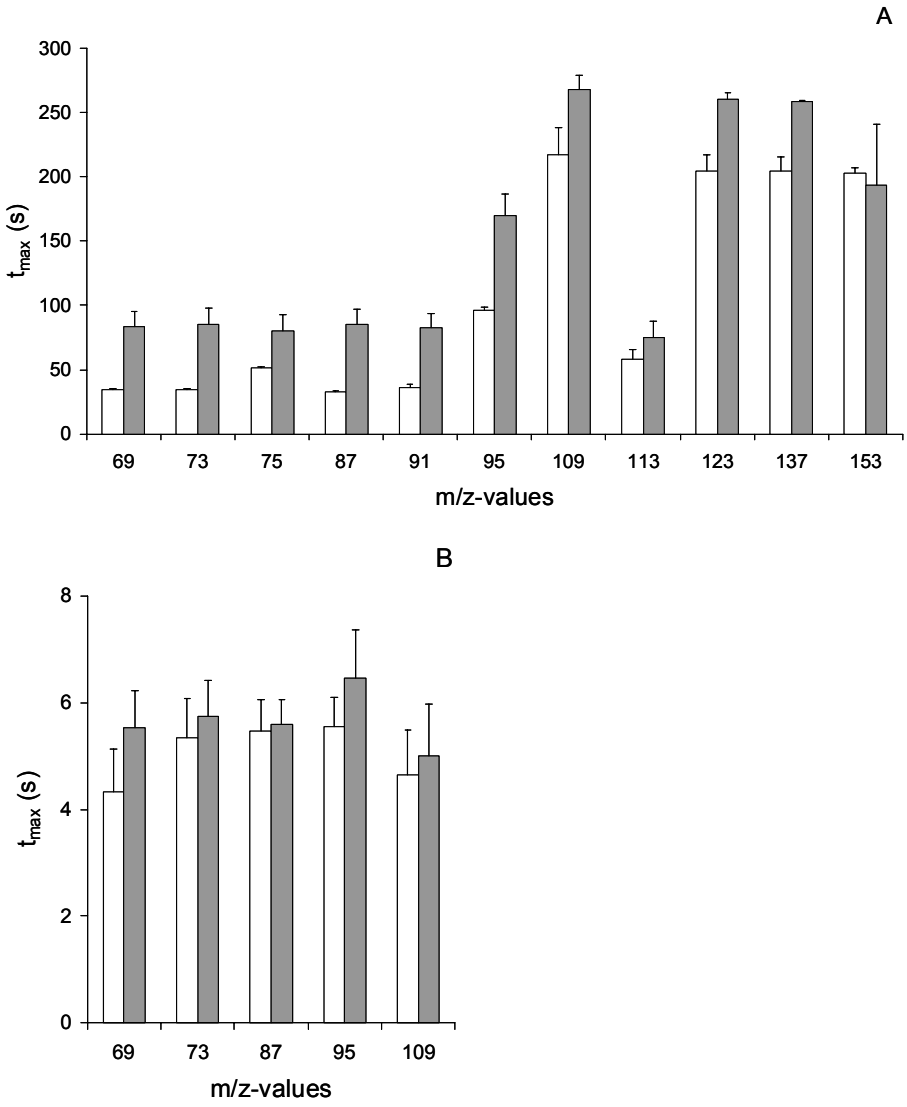

Figure 5.7. t_{max} *in vitro* (A) and *in vivo* (B) of compounds released from French fries produced according to conventional process (white) and the alternative process (grey). Error bars represent the standard error.

In conclusion, with MS-Nose it is possible to identify and follow the release of several flavour compounds from French fries both with assessors and with a mouth model system. Longer

frying times resulted in a higher I_{max} for all compounds. Addition of salt caused a decrease of t_{max}, while an increase of t_{max} was found for the release of flavour compounds from French fries produced with the alternative process. Trends observed in experiments with assessors were found to be statistically significant with the mouth model system. Therefore, a combination of *in vivo* and *in vitro* measurements gives a synergy.

5.4 ACKNOWLEDGMENTS

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Chapter 6

Towards a kinetic model for the formation of acrylamide in a glucose-asparagine reaction system

This chapter has been submitted for publication by JJ Knol, WAM van Loon, JPH Linssen, A-L Ruck, MAJS van Boekel, and AGJ Voragen. The first two authors contributed equally.

ABSTRACT

A kinetic model for the formation of acrylamide in a glucose-asparagine reaction system is proposed. Equimolar solutions (0.2 M) of glucose and asparagine were heated at different temperatures (120–200 °C) at pH 6.8. Besides the reactants, acrylamide, fructose, and melanoidines were quantified after predetermined heating times (0–45 min). Multiresponse modelling using non-linear regression with the determinant criterion was used to estimate model parameters. The proposed model resulted in a reasonable estimation for the formation of acrylamide in an aqueous model system, although the behaviour of glucose, fructose, and asparagine was slightly underestimated. The formation of acrylamide reached its maximum, when the concentration of sugars was reduced to about zero. This supported previous research, showing that a carbonyl source is needed for the formation of acrylamide from asparagine. Furthermore, it is suggested that acrylamide is an intermediate of the Maillard reaction rather than an end product.

6.1 INTRODUCTION

In April 2002 Tareke *et al*.[1] reported that several heat-processed foods contain relatively high amounts of acrylamide. These results were confirmed by other research groups: fried and baked potato products were found to contain the highest amounts of acrylamide followed by cereal products, whereas only low amounts were detected in meat products.[2-4] A high amount in foods is of major concern as acrylamide is known to be a neurotoxic, genotoxic, and carcinogenic compound in animals,[5] which is classified by the IARC [6] as a probable human carcinogen.

About half a year later the suggestion was published that acrylamide is formed in the Maillard reaction, and that asparagine is the precursor.[7-9] Further elucidation of the pathway using ^{13}C-labeled isotopes showed that asparagine needs a carbonyl source to form acrylamide.[10,11] According to Friedman [5] the proposed mechanisms predict that acrylamide may result from the general reaction of asparagine with any aldehyde or ketone. Simultaneously, many researchers focused on optimisation of methods for determination of acrylamide. A review about this subject was published by Wenzl *et al*.[12] Evaluation of the health risk resulted in the recommendation that intake levels of acrylamide should be reduced to protect health, although there is no direct risk on cancer with the current intake of about 35 μg/day per person.[13,14] Possible ways to reduce the formation of acrylamide include reducing the temperature, reducing precursors during processing, and influencing the pathway of formation by changing the pH.[15-17] More information on research, analysis, formation and control of acrylamide is available in an extensive review that was published recently.[18]

The Maillard reaction is highly complex, and cannot be described with simple reaction kinetics. To better understand mechanisms behind the formation of acrylamide, an advanced approach is necessary.[19] Kinetic modelling, using multiresponse models, has proven to be a useful tool to enable further unravelling of reaction mechanisms in the Maillard reaction.[20,21] Knowledge of kinetics provides the tool to predict the effect of certain time-temperature combinations in a quantitative way.

Model systems of asparagine and a carbonyl such as glucose, both dry and in aqueous solutions, have been used mainly to study the pathway of acrylamide formation.[3,22] The yield of acrylamide was about 1000 mg/kg, and a wide range of other compounds (e.g. melanoidines) was found. Furthermore, an effect of time and temperature on both formation and degradation of acrylamide has been found. Kinetic modelling of acrylamide formation, however, has not been published so far. Therefore, the aim of this study was to attempt to model the formation of acrylamide in a glucose-asparagine reaction system at different time-temperature combinations.

6.2 MATERIAL AND METHODS

Chemicals

The following compounds were obtained commercially: D-glucose, D-fructose, Na_2HPO_4, KH_2PO_4 (Merck, Darmstadt, Germany); L-asparagine (Fluka, Buchs, Switzerland). All chemicals used in this study were of analytical grade.

Preparation of reaction mixtures

Equimolar solutions of glucose and asparagine (0.2 M) were prepared in phosphate buffer (10 ml, 0.1 M, pH 6.8). Samples were heated in screw-capped glass tubes (Schott, 16 × 160 mm) at 120, 140, 160, 180 and 200 ºC in an oil bath. At predetermined heating times (0, 1, 2, 4, 9, 15, 30, and 45 min) samples were taken and immediately cooled in ice and stored at –20 ºC prior to analysis. Experiments were carried out in triplicate.

Analysis of acrylamide

Acrylamide was determined by HPLC after dilution in millipore water (1:10) and centrifugation for 5 min at 16000 g. The HPLC system consisted of a P4000 pump, an AS3000 autosampler, and a UV3000 detector (Thermo Separation Products, San Jose, CA). A Synergi 4µ Hydro Reversed Phase C18 column (80 Å, 250 × 2.00 mm) with AJO-4286 guard column (Phenomenex, Aschaffenburg, Germany) was used at 20 ºC. Samples (20 µl) were eluted isocratically with a solution containing 1% of methanol and 99% of 5 mM heptanesulfonic acid in millipore water at a flow rate of 0.2 ml/min. Acrylamide (t_r = 6.2 min) was detected by its

absorbance at 200 nm with a UV-detector, and quantified by the external standard procedure using a calibration curve.

Analysis of sugars

The diluted samples (1:10) were analysed for sugars by HPLC (see Analysis of acrylamide) using the method of Martins *et al*.[23] An ion-exchange column (ION-300, Interaction Chromatography Inc., San Jose, CA) with guard column was used for the analysis at 85 ºC. Sulphuric acid (2.5 mM) in millipore water was used as the eluens with a flow rate of 0.4 ml/min. Sugars were detected by monitoring the refractive index and quantified by the external standard procedure using a calibration curve.

Analysis of asparagine

Samples were diluted 1:1000 with millipore water and the EZ:faast Amino Acid Analysis Kit (Phenomenex, Aschaffenburg, Germany) was used for determination of asparagine.[24] Norvaline was added as an internal standard (20 nmol) before sample preparation. After sample preparation, samples were analysed using a Carlo Erba GC5300 system (Interscience BV, Breda, The Netherlands) on a Zebron Amino Acid column (10 m × 0.25 mm) that was included in the kit. Samples (2.5 µl) were injected onto the column at 250 ºC (split ratio 1:15). The oven temperature started at 110 °C, and was programmed to heat to 250 ºC at a rate of 20 ºC/min, followed by a 1 min isothermal hold. The external standard procedure was used for quantification.

Analysis of melanoidines

Quantification of melanoidines was performed by measuring the absorbance at 470 nm using a spectrophotometer (UV-1601, Shimadzu, Kyoto, Japan). When necessary the samples were diluted with millipore water. The concentration of melanoidines was calculated using the Lambert-Beer equation with an extinction coefficient of 282 l/(mol·cm);[25] a value derived for melanoidines formed from glucose and asparagine. The concentration of melanoidines is thus expressed as moles of sugar incorporated in the brown polymers.

Kinetic modelling

A kinetic model was derived from the proposed reaction network taken from Stadler *et al*.[26] that is shown in Figure 6.1.

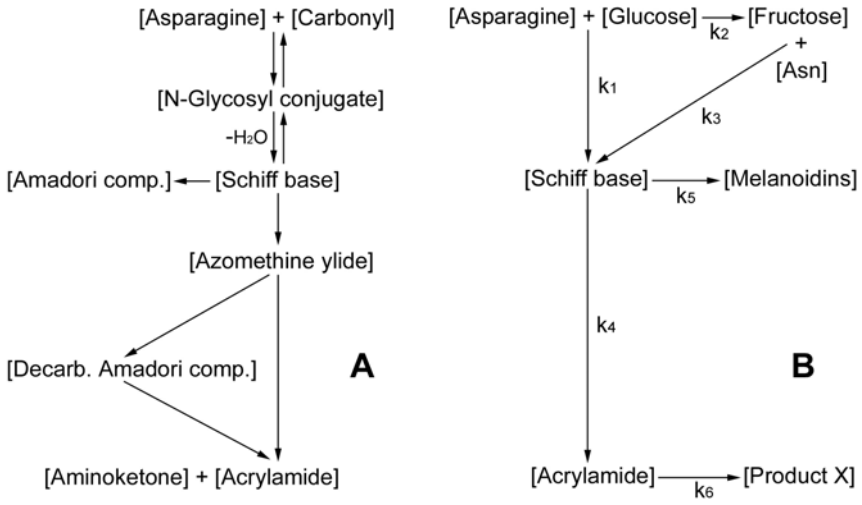

Figure 6.1. Reaction network for the formation of acrylamide from asparagine through early Maillard reaction adapted from Stadler *et al*.[26](A), and simplified reaction network for the formation of acrylamide from asparagine and glucose/fructose through early Maillard reaction (B). Decarboxylated Amadori compound (Decarb. Amadori comp.); Asparagine (Asn); Assumed product(s) formed from acrylamide (Product X).

Our arguments for using the reaction network published by Stadler *et al*.[26] and the steps taken to derive a kinetic model will be discussed further on. For each reaction step a differential equation was set up, and these were translated into a mathematical model. The differential equations were solved by numerical integration. For both numerical integration and parameter estimation the software package Athena Visual Studio v. 10.0 [27] was used. The parameters of the model, i.e., the rate constants and activation energies were estimated by non-linear regression using the determinant criterion.[20] For modelling individually measured concentrations were used (measured in triplicate). For the visualization of the experimental results (Figure 6.2) the average values with their standard deviation (represented by the error bars) were used.

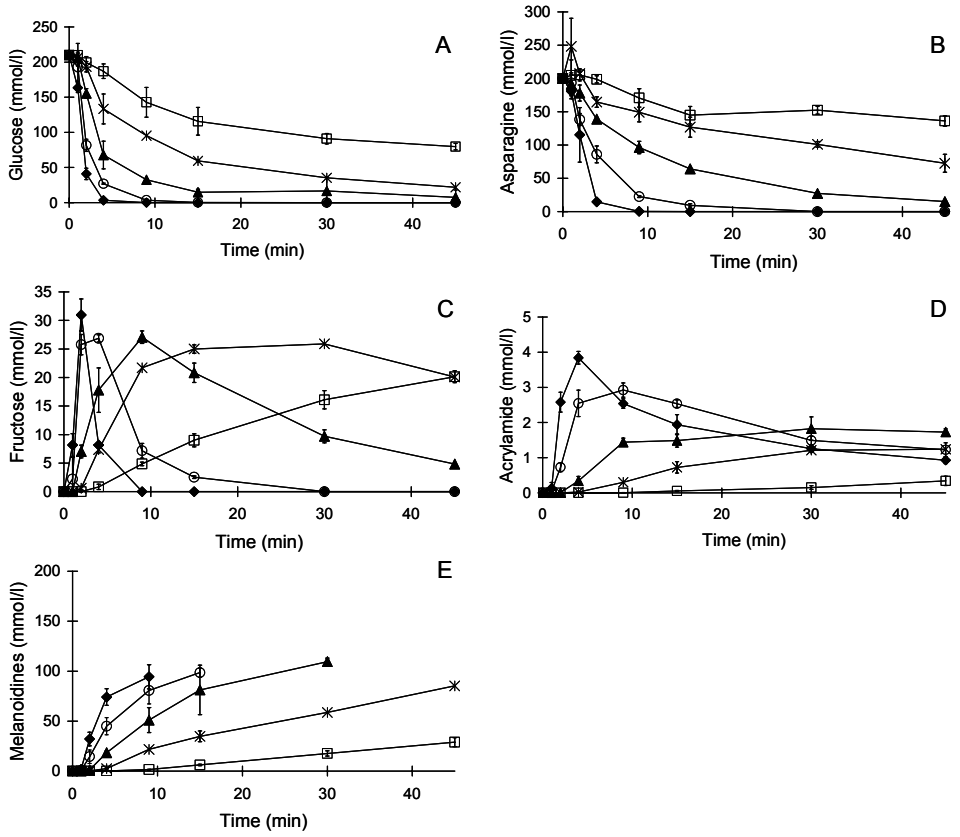

Figure 6.2. Experimental data of glucose-asparagine (0.2 mol/l, pH 6.8) aqueous reaction system heated at 120 (□), 140 (✱), 160 (▲), 180 (○) and 200 °C (◆) showing glucose (A), asparagine (B), fructose (C), acrylamide (D), and melanoidines (E).

6.3 RESULTS AND DISCUSSION

Identification and quantification of reactants and main products

During heating of the glucose-asparagine reaction mixtures the concentrations of the reactants decreased over time. As expected the rate of degradation of glucose and asparagine increased with temperature. At 180 and 200 ºC a complete loss of glucose was observed after 9 and 5 min,

respectively (Figure 6.2A). The loss of asparagine (Figure 6.2B) was slower compared to the loss of glucose. A complete loss of asparagine was measured at 180 and 200 °C after 30 and 9 minutes, respectively. The effect that the loss of sugar was faster than the loss of amino acid is in line with what has been found in a glucose-glycine reaction system by Martins and Van Boekel.[20] The slower loss can possibly be explained by the regeneration of asparagine from the initial condensation products such as the Amadori rearrangement product and the possible formation of diglucosylamine.[20]

As fructose and mannose are known to be formed from glucose by isomerisation,[23] some formation of these compounds was expected. Analysis showed no formation of mannose, but fructose was indeed formed (Figure 6.2C). This corresponds with findings of Brands and Van Boekel [28] and Martins and Van Boekel [20] where only fructose was found as isomerisation product of glucose. At 160, 180 and 200 °C there was a clear maximum in the formation of fructose at 9, 4 and 2 minutes, respectively. For the reaction mixtures heated at 180 and 200 °C these maximum values were followed by a complete loss after 30 and 9 minutes, respectively. The decrease in fructose concentration can be explained by the reversible isomerisation reaction between glucose and fructose so that fructose reforms back into glucose, which is then consumed, but it is also quite likely that fructose participates in the formation of acrylamide.[29-31]

The initial rate of formation of acrylamide increased with temperature (Figure 6.2D). At 140 and 160 °C the increase in acrylamide concentration was followed by a steady state in which the formation of acrylamide was probably in equilibrium with its degradation. At 180 and 200 °C the increase was followed by a fast decrease. The maximal acrylamide formation at 180 and 200 °C corresponded with the time, at which the concentration of glucose and fructose reached zero (Figure 6.2A and 6.2C). This is in line with the findings of Yaylayan and co-workers,[10] who showed that asparagine needs a carbonyl source to form acrylamide. The decrease in acrylamide can be explained by its reactive nature. The increase and subsequent decrease of the acrylamide concentration at 180 and 200 °C is a typical behaviour for an intermediate.[20] Acrylamide may have polymerised or reacted further in Michael type addition reactions.[26] These pathways have not been fully elucidated and further research in this area is necessary to expand the reaction network of the Maillard reaction between asparagine and glucose.

Melanoidines are known as the main end products of the Maillard reaction. The structure of these brown nitrogenous polymers and co-polymers is largely unknown, which makes quantification difficult. Previous studies have shown that it is possible to relate the absorbance to the number of sugar molecules incorporated in the melanoidines in aqueous model systems.[20,25,32] At 160, 180 and 200 °C we observed after some time the formation of insoluble particles, which are probably high molecular weight melanoidines. The absorbance measurements were hindered by the scattering effect of these particles. Moreover, the values for absorbance decreased during formation of these particles, causing an underestimation of the melanoidines concentration. Because of this, we excluded the results for the reaction mixtures where these solid compounds were found. This was the case for the reaction mixtures heated for 45 min at 160, 180 and 200 °C, for 30 min at 180 and 200 °C and 15 min at 200 °C. Considerable browning was observed in samples during heating. The induction time, during which no browning was detected, decreased with increasing temperature (Figure 6.2E). Furthermore, the formation of acrylamide could not be associated directly with the degree of colouring of the reaction mixtures at 160, 180 and 200 °C after 15, 9 and 4 minutes, respectively. This is due to their difference in status: acrylamide is an intermediate, whereas melanoidines are the main end products of the Maillard reaction. The relationship between acrylamide and colour formation in foods found in yeast-leavened wheat bread by Surdyk *et al*.,[30] must have been induced by effects such as concentration gradients, diffusion and evaporation and the presence of other compounds such as other amino acids and sugars. Consequently, our proposed kinetic model only applies to an aqueous model system.

Proposal of a kinetic model based on a reaction network

By analysing the reactant degradation and the formation of the main products in the Maillard reaction between glucose and asparagine a kinetic model could be proposed. The mathematical model derived from the kinetic model was then confronted with the experimental data to test the hypothesized model. Several reaction networks for the formation of acrylamide in foods have been proposed. These publications have revealed the Maillard reaction as the major reaction pathway involved.[3,7-9] The hypothesis proposed by Mottram *et al*.[7] emphasizes the pathway of Strecker degradation. The hypothesis proposed by Stadler *et al*.[8], however, pointed towards

glycoconjugates such as N-glycosides, formed in the early Maillard reaction as key intermediates. A recent publication by Stadler *et al*.[26] supports their hypothesis as well as the work published by Zyzak *et al*.[11] and Yaylayan *et al*.[10] Furthermore, Stadler *et al*.[26] suggest that the mechanism proposed by Mottram *et al*.[7] is not a main one. We did not pursue the identification and quantification of all these suggested intermediates in this study and, therefore, we are not able to shed more light on this matter. However, we chose the reaction network proposed by Stadler *et al*.,[26] shown in Figure 6.1A, as initial basis for the proposal of a kinetic model, as their proposed reaction network has been more elaborately described in recent literature.[8] To fit the model to the experimental data, this reaction network was first adapted to reduce the number of parameters. Because the intermediates (e.g. N-glycosyl conjugate, azomethine ylide) were not analysed and quantified in our experiments, the number of parameters was relatively high to the number of measured responses. Secondly, the new reaction network proposed in Figure 6.1B also takes the measured responses for fructose and melanoidines and the observed loss of acrylamide into account. The formation of fructose was suggested by including the reversible isomerisation reaction between glucose and fructose. Furthermore, the reaction between asparagine and fructose was added, since fructose is also a reactant in the formation of acrylamide.[29-31] The formation of melanoidines was suggested to result from further reaction of Schiff base, and the loss of acrylamide was accounted by the putative formation of hitherto unknown product(s).

Test of the hypothesized mechanism

The proposed reaction model presented in Figure 6.2B was translated into a mathematical model. For each reaction step a differential equation was set-up using the law of mass action, and the obtained differential equations were solved by numerical integration. The temperature dependence, which plays a major role in the Maillard reaction, was also taken into account by including an Arrhenius relationship between the rate constants (k) of the different reactions. The Arrhenius equation

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \tag{6.1}$$

where k_0 is the so-called frequency factor, R the gas constant (8.314 J/(mol·K)), E_a the activation energy (J/mol) and T the absolute temperature (K), was reparameterised to avoid statistical problems in estimation [33] as follows:

$$k = X \exp(-YE_a) \tag{6.2}$$

where X and Y are, respectively:

$$X = k_0 \exp\left(\frac{-E_a}{RT_{av}}\right), \tag{6.3}$$

$$Y = \frac{1}{R}\left(\frac{1}{T} - \frac{1}{T_{av}}\right), \tag{6.4}$$

and:

$$T_{av} = \frac{\Sigma T}{n}. \tag{6.5}$$

The model was fitted to the data obtained at 120, 140, 160, 180 and 200 °C at pH 6.8 simultaneously by substituting equation (6.2) for the rate constants (Figure 6.3).

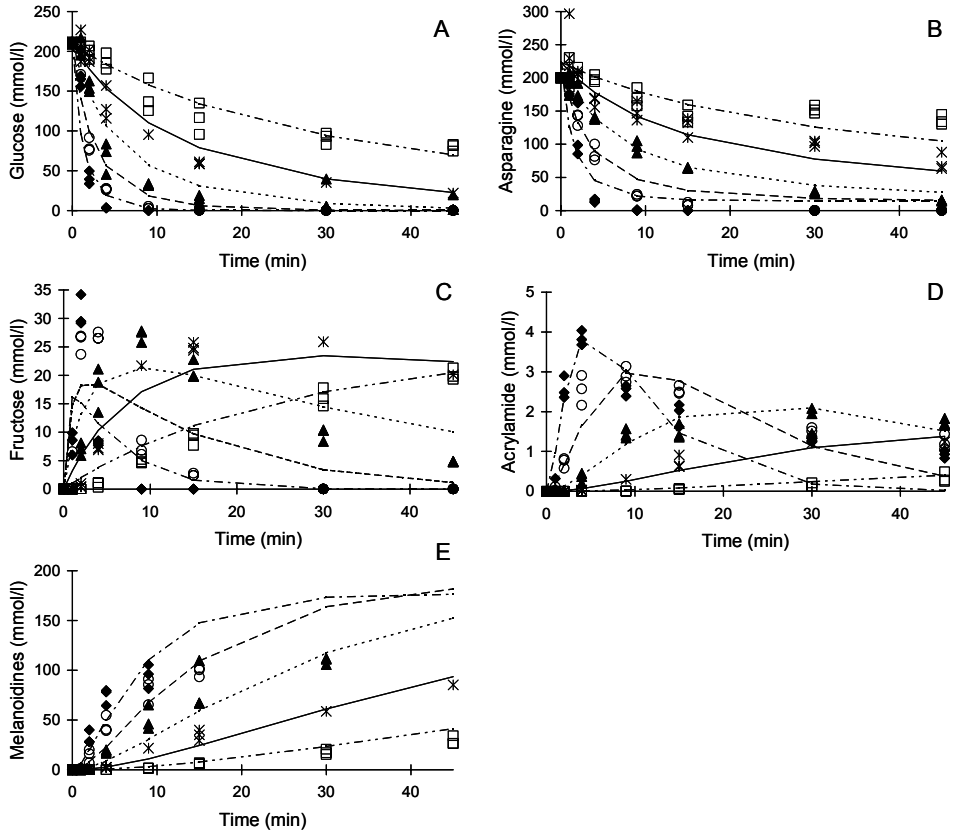

Figure 6.3. Model fit (lines) to experimental data (symbols) of glucose-asparagine (0.2 mol/l, pH 6.8) aqueous reaction system heated at 120 (□;– – —), 140 (✱; ———), 160 (▲; – – –), 180 (○; — —), and 200 °C (◆; — - —) showing glucose (A), asparagine (B), fructose (C) acrylamide (D), and melanoidines (E).

At the lower reaction temperatures (120 and 140 °C) quite a good fit was observed for all compounds (Figures 6.3A-E). For the acrylamide and melanoidines concentrations the model fits the data well at all temperatures (Figure 6.3D and E). However, the good fit for the melanoidines concentration may have been partially caused by the lack of data for the higher temperatures. For the estimation of the acrylamide concentration the model was not restrained by experimental data for the products formed in the degradation reaction from acrylamide and,

therefore, the model was able to fit the loss of acrylamide (k_6) to the experimental observations for acrylamide. More knowledge about the reaction products from acrylamide would validate the estimated rate constants for the formation and loss of acrylamide.

The observed lack of fit for the individual responses was rather high, especially for fructose and at the higher temperatures. The model underestimated the decrease in glucose concentration, especially during the first 10 minutes (Figure 6.3A). The increase in fructose was also underestimated, but the model predicted the tendencies as found in the experimental observations (Figure 6.3C). The same goes for asparagine where there was an underestimation for the decrease (Figure 6.3B). These underestimations are undoubtedly caused by the limitations of the present model. Reactions of glucose and fructose are limited to the isomerisation reaction and the reaction with asparagine to form the Schiff base. The model does not take into account the degradation of sugars to carbohydrate fragments and the formation of compounds via the Strecker degradation route. Therefore, this model is currently under further investigation. Nevertheless, the results show already some remarkable phenomena that are worth discussing. The estimated parameters, the rate constants and activation energies, are shown in Table 6.1.

Table 6.1. Estimates of rate constants (k) at 120, 140, 160, 180 and 200ºC and activation energies (E_a) ± 95% Highest Posterior Density (HPD) interval as found by kinetic modelling for the proposed kinetic model.

k [A]	120 ºC	140 ºC	160 ºC	180 ºC	200 ºC	E_a (kJ/mol)
k_1	0.131 ± 0.025	0.308 ± 0.049	0.668 ± 0.13	1.35 ± 0.36	2.58 ± 0.89	57.6 ± 8.0
k_2	4.98 ± 1.2	16.7 ± 3.0	50.1 ± 9.6	136 ± 35	341 ± 114	81.7 ± 8.6
k_3	0.082 ± 0.045	0.369 ± 0.14	1.45 ± 0.44	5.04 ± 1.6	15.8 ± 6.4	102 ± 14
k_4	0.176 ± 0.081	0.712 ± 0.23	2.53 ± 0.51	8.05 ± 1.2	23.2 ± 4.3	94.4 ± 11
k_5	15.7 ± 3.5	28.4 ± 4.6	48.7 ± 5.9	79.6 ± 8.9	125 ± 16	40.1 ± 5.0
k_6	7.96 ± 5.1	28.1 ± 13	88.1 ± 25	250 ± 45	650 ± 136	85.1 ± 14

[A] All k-values are expressed as $\cdot 10^{-3}$/min

The rate constants for the different reaction temperatures have been derived from the estimated values found for X. The estimated values of X are the same as the derived values for the rate

constants at 160 °C as T_{av} in this case is 160 °C. The temperature dependence is consistent for all six reactions, but the precision of estimation for the parameters is low. The average 95%-highest posterior density interval is about ± 27% for the rate constants and ± 11% for the activation energies. The activation energy for the formation of the Schiff base from fructose and asparagine is about two times higher than the activation energy for the same formation reaction with glucose and asparagine as reactants, suggesting that the contribution from fructose becomes more important at higher temperatures. The rate of the Schiff base formation reaction from fructose and asparagine (k_3) increases, therefore, much faster with increasing temperature than the rate constant of reaction 1 (k_1). At 120 °C k_3 is 35% lower than k_1, but at 180 °C k_3 is two to three times higher than k_1. This is consistent with the observations by Robert *et al*.[29] that fructose is more efficient in the formation of acrylamide than glucose by a factor of about three at 180 °C. The higher reactivity of fructose with asparagine in the formation of the Schiff base could make the reversible isomerisation step of fructose to glucose insignificant. Therefore, model discrimination was performed for our proposed model with or without the reversible isomerisation reaction from fructose to glucose. Model discrimation can be used to provide information about the most plausible model.[20] In this case we used the Akaike Criterion (the model with the lowest value is preferred) and the posterior probability (the model with the highest posterior probability is preferred) to assess the most plausible model.[34,35] The results from our test, shown in Table 6.2, support the model without the reversible isomerisation reaction.

Table 6.2. Model discrimination results for our proposed model with (A) or without (B) the reversible isomerisation reaction from fructose to glucose.

Model	*p*	SS	*n*	AIC_f	ΔAIC_c	PPB	PPS
A	16	$1.32 \cdot 10^5$	600	6505.2	27.3	-89.83	0.234
B	14	$1.29 \cdot 10^5$	600	6477.9	0.0	-89.33	0.757

p (number of parameters), SS (Residual Sum of Squares), *n* (number of data points including the replicates), AIC_c (Akaike Criterion), ΔAIC_c (AIC_c difference taking the smallest value as reference), PPB (Log10 of Posterior Probability), and PPS (Normalized Posterior Probability Share).

The aim of this study was to work towards a reaction model for the formation of acrylamide in the Maillard reaction of glucose and asparagine at initial pH of 6.8. Despite the current

underestimation for the behaviour of sugars and asparagine, the proposed model gives a reasonable estimation for the formation of acrylamide in an aqueous model system. The kinetic model supports the observations that for the formation of acrylamide from asparagine a carbonyl source is needed,[11] and our results suggest an important role for fructose, especially at the lower temperatures. Fructose is invariably formed from glucose isomerisation. Furthermore, the experimental observations and the kinetic modelling suggested that acrylamide is not an end product in the Maillard reaction. The behaviour of acrylamide suggests that it is an intermediate. The multiresponse model derived in this study is a first step into the realisation of a tool that can be used to predict how acrylamide reduction in foods containing asparagine and reducing sugars can be accomplished. Further research is on the way to determine intermediate reaction products in order to extend the kinetic model. In addition, the formation of compounds via the Strecker degradation route and the degradation of sugars into carbohydrate fragments will be investigated to improve the current kinetic model in estimating the behaviour of sugars and asparagine.

6.4 ACKNOWLEDGMENTS

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Chapter 7

Antiradical power gives insight in early lipid oxidation events at frying conditions

This chapter has been submitted for publication by WAM van Loon, JPH Linssen, A Legger, and AGJ Voragen.

ABSTRACT

Early lipid oxidation events were studied at frying conditions by following antiradical power (ARP). The 2,2-diphenyl-1-picrylhydrazyl radical (DPPH•) test was used to determine the ARP. As oil does not dissolve completely in methanol, which is generally used for the DPPH• test, butanol was used instead. Changing the solvent did not influence the value of the ARP. The decrease of the ARP correlated well with the increase of the peroxide value for soybean oil heated at 110 °C. Sensory analysis showed that rancidity of soybean oil and frying oil, heated at 180 °C, was perceived at an earlier stage than the ARP decreased. Once the oil was perceived as rancid, the intensity of rancidity did not change significantly upon further heating. The ARP of soybean oil was found to decrease faster at 110 °C than at 180 °C, suggesting different mechanisms of radical formation. The total polar compounds of frying oil, in which French fries were fried, did not differ significantly from frying oil that was solely heated. However, frying of French fries caused more hydrolysis of the oil, while the ARP decreased faster when the oil was solely heated.

7.1 INTRODUCTION

Frying is one of the most popular applications to prepare food throughout the world. The quality of the frying oil strongly influences the quality of the food fried in it.[1] During frying, the physical and chemical properties of the oil change considerably because of hydrolysis, oxidation and thermal alteration,[2] and this directly influences the functional, sensory, and nutritional quality of the oil.[3] The kinetics of these degradation reactions are influenced by several factors such as food composition, food to oil ratio, frying temperature, and oil composition.[4]

Lipid oxidation is initiated by removal of the energetically weakest bound proton of an unsaturated fatty acid, resulting in the formation of an alkyl radical. By reacting with oxygen, peroxy radicals are formed. These can react with other fatty acids to form hydroperoxides, the primary oxidation products, and new alkyl radicals, showing the autocatalytical character of the propagation reaction in lipid oxidation. Hydroperoxides are unstable and decompose in many steps to a wide variety of secondary products. Several secondary oxidation products such as aldehydes and ketones are known to cause a rancid off-flavour.[2] It is, however, difficult to measure oxidation in a quantitative way. The peroxide value (PV) is useful to monitor the initial stage of oxidation, because primary oxidation products are measured.[3] However, the use of the PV as a measure for lipid oxidation is limited, because it decreases as oxidation proceeds due to rapid decomposition of hydroperoxides. Moreover, hydroperoxides are highly unstable at elevated temperature. Therefore, the PV is not suitable to follow lipid oxidation at frying conditions.[5] The TBA-test measures the secondary oxidation product malondialdehyde, but this compound is only formed from fatty acids with at least three double bonds.[6] Many other secondary oxidation products are volatile and, therefore, more suitable to study underlying mechanisms of formation than for quantitative analysis.[7] Tests that measure secondary oxidation products, such as the *p*-anisidine value are, therefore, not useful to study early lipid oxidation at frying temperature.

The 2,2-diphenyl-1-picrylhydrazyl radical (DPPH•) test has been used to measure the antiradical power (ARP) of antioxidants.[8] Recently, the test was modified to measure the ARP of oil and oil fractions. Ethyl acetate was used as a solvent instead of methanol, because oil does not dissolve

well in methanol. For most oils the methanolic fraction showed a lower ARP than the remaining lipidic fraction.[9,10] In fact, this is an opposite strategy: instead of measuring oxidation products directly, the decrease of antioxidative capacity is determined. However, little is known about the decrease of ARP in relation to oxidative processes in oil.

In the present paper early lipid oxidation events were studied at frying conditions by following the ARP. The ARP was studied in relation to the formation of primary and secondary oxidation products. Also, the ARP was followed in oil that was solely heated in comparison with oil in which French fries were fried.

7.2 MATERIALS AND METHODS

Materials

Two types of oil were used in the experiments: partially hydrogenated vegetable frying oil (Remia, Den Dolder, The Netherlands) and soybean oil (Levo BV, Franeker, The Netherlands). The frying oil consisted of 15.6% saturated, 72.1% monounsaturated, and 12.3% polyunsaturated fatty acids, and the soybean oil consisted of 16.5% saturated, 24.4% monounsaturated, and 59.1% polyunsaturated fatty acids.

Determination of ARP

The ARP was determined with the DPPH•-test. The procedure of Brand-Williams *et al*.[8] was followed with some modifications. As oil does not dissolve completely in methanol, butanol was used instead. Other solvents such as ethyl acetate have been used successfully in the DPPH•-test,[9,10] but the use of butanol has not been reported. To check whether this does not affect the results, the ARP of three antioxidants (α-tocopherol, oleuropein, and ascorbyl palmitate) was determined both in methanol and in butanol.

For all spectrophotometric analysis a UV–1601 spectrophotometer (Shimadzu, Kyoto, Japan) was used, and the absorbance was measured at 515 nm in glass cuvettes (1 × 1 × 4.5 cm, Hellma Benelux BV, Rijswijk, The Netherlands) equipped with a stopper to prevent evaporation of the solvent. The antiradical activity (effective concentration, EC50) was defined as the amount of oil

or antioxidant (g/g DPPH•) necessary to decrease the initial DPPH• concentration by 50%. The ARP is the reciprocal of this value, so that the larger the ARP, the more effective the antioxidant. Oil samples were dissolved in butanol (28 g/l) and dilutions were made (1:1, 1:2, 1:4, and 1:8). Of these solutions 2.7 ml was added to 0.3 ml of DPPH• in butanol (237 mg/l butanol) and the absorbance was measured every 90 s for 90 min. For the initial concentration 2.7 ml of butanol was added to 0.3 ml of the same DPPH• solution. Because DPPH• is not very stable, a calibration curve (0–25 mg/l) was used to determine the initial concentration of every analysis. The ARP of antioxidants was determined in a similar manner. However, the concentration of the antioxidants was lower (about 16 mg/l), because the ARP was expected to be higher than that of oil. The absorbance was measured for 30 min, until steady state was reached. All ARP values were based on at least four dilutions.

Relation between ARP and PV

To correlate the formation of hydroperoxides with the decline of the antiradical activity, soybean oil was heated at 110 °C. This temperature was chosen, because hydroperoxides are very unstable at 180 °C. Separate open samples bottles were used to heat the oil for 0, 21, 45, 93, 141, and 189 h. After heating, samples were stored at –18 °C under nitrogen until analysis of ARP and PV. For the determination of the PV the official AOCS method Cd 8-53 [11] was used.

Relation between ARP and sensory perceived rancidity

Frying oil and soybean oil (5 l) were heated 8 h per day at 180 °C for 8 days in a Princess Classis household fryer (Princess Household Appliances, Middelharnis, The Netherlands). Samples of 100 ml were taken every day after 3 and 8 h, and stored at –18 °C under nitrogen until analysis of ARP and rancidity. An analytical panel was used to evaluate oil samples on rancidity. The panel consisted of 18 assessors, 7 male and 11 female in the age of 20–25 who regularly participate in sensory evaluations. A training session was carried out to make the assessors familiar with the offered samples. Samples of both oils were offered to the panel at ambient temperature after a total heating time of 0, 8, 19, 32, 48, and 64 h. Because the colour of the oil changed during heating, a black colorant (Sudan black B, Janssen Chimica, Geel, Belgium) was added to mask colour differences. During the evaluation assessors were asked to smell the samples and put a mark for rancidity on a 150 mm line scale using a computer program

written in Pascal. A fresh and a very rancid oil sample (heated for 72 h at 180 °C) were offered to mark, respectively, the left and right anchor point of the scale. Scores were calculated by measuring the distance in mm from the left anchor point.

Comparison of oil deterioration by solely heating and by heating with intermediate frying of French fries

Frying oil (3 l) was heated 8 h per day at 180 °C for 8 days in two Princess Classic household fryers. In one fryer the oil was solely heated, and in the other fryer every hour an amount of French fries (par-fried and frozen, obtained from a local supermarket) was fried for 5 min. The starting amount of French fries was 200 g, but decreased in time in order to keep the product to oil ratio constant. The amount of oil decreased, because oil was taken up by the product and by sampling. Samples (15 ml) were taken every 2 h and stored at –18 °C under nitrogen until analysis of ARP, polar compounds, colour, and free fatty acids (FFA). Polar compounds were measured according to the method of Schulte *et al*.,[12] and for FFA the official AOCS method Ca 5a-40 [11] was used. The colour was measured with a Dr. Lange Tricolor LFM3 Colorimeter (IMA Instruments, Kesteren, The Netherlands), and expressed as L*, a*, and b*. The L*-value represents black–white (0–100), the a*-value green–red (negative–positive), and the b*-value blue–yellow (negative–positive). The analyses for polar compounds, colour, and FFA were carried out in duplicate.

Statistical evaluation

All statistical analyses were performed using SPSS 10.0.7 (SPSS Benelux BV, Gorinchem, The Netherlands). For correlations the Pearson correlation was calculated. Sensory data were evaluated with General Linear Model. Z-values $\geq |2|$ were considered as outliers, and a post hoc test according to Tukey was performed to identify differences at a significance level of $\alpha \leq 0.05$. General Linear Model was also used to determine whether a slope was significantly different for two variables at $\alpha \leq 0.05$.

7.3 RESULTS AND DISCUSSION

ARP of antioxidants in methanol and butanol

To determine whether the use of methanol or butanol affects the antiradical activity, the EC50 and ARP of three antioxidants was determined using both solvents. In Table 7.1 it can be seen that the results of the EC50 values were in good agreement for the two solvents.

Table 7.1. EC50 and ARP of three antioxidants in methanol and butanol.

Antioxidant	EC50		ARP	
	methanol	butanol	methanol	butanol
α-tocopherol	0.27	0.24	3.7	4.1
oleuropein	0.27	0.29	3.7	3.4
ascorbyl palmitate	0.23	0.26	4.3	3.9

Literature values of the ARP for tocopherol (4.0) and the EC50 value of oleuropein (0.29) were in the same order.[8,13] The ARP or EC50 of ascorbyl palmitate could not be found nor calculated from the literature. According to Gopinath *et al*.[14] the reduction of DPPH• by ascorbyl palmitate was not significantly different from that of ascorbic acid. An ARP value of 3.7 was found for ascorbic acid,[8] which is in the same range as what we found for ascorbyl palmitate.

Relation between ARP and PV

A temperature of 110 °C was chosen to compare ARP and PV instead of 180 °C, because hydroperoxides decompose above 150 °C. Determination of the PV of oil heated at 180 °C would, therefore, only represent hydroperoxide formation during storage. The results for ARP and PV of soybean oil heated at 110 °C are shown in Figure 7.1.

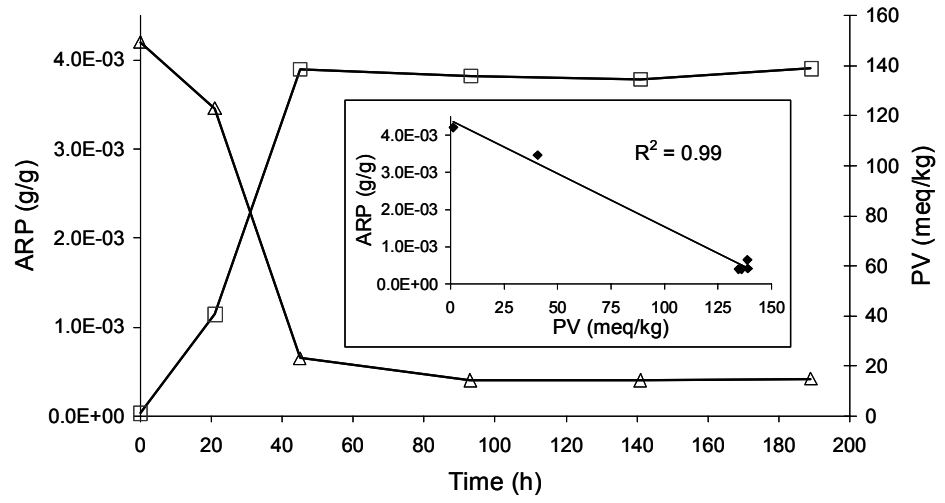


Figure 7.1. ARP (Δ) and PV (□) of soybean oil heated at 110 °C. The correlation between ARP and PV is inserted.

The ARP decreased at around the same time as primary oxidation products were formed. A correlation coefficient between ARP and PV of –0.99 was found. Antioxidants in oil react with radicals, and the PV was expected to increase only when not enough antioxidant was left to compensate for the radical formation. On the other hand, the formation of peroxides is a chain reaction that occurs so rapidly that peroxide formation and radical scavenging start, apparently, almost simultaneously.

Relation between ARP and sensory perceived rancidity

Figure 7.2 shows the ARP and perceived rancidity of soybean oil and frying oil, heated at 180 °C.

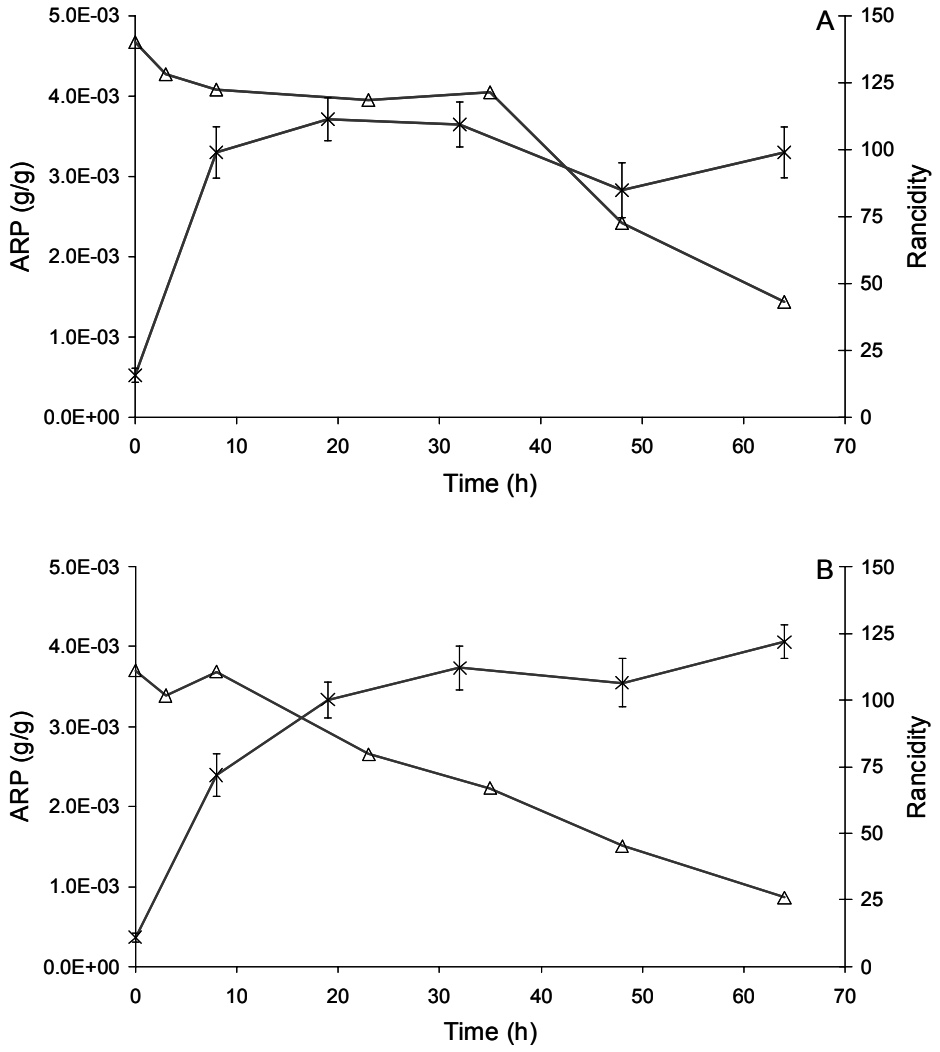


Figure 7.2. ARP (Δ) and sensory perceived rancidity (×) of soybean oil (A) and frying oil (B) heated at 180 °C.

The ARP of soybean oil decreased slower at 180 °C than at 110 °C (Figure 7.1). This seems to contradict with the general law that chemical reactions, such as oxidation, are accelerated by an increase in temperature. However, at high temperatures hydroperoxides decompose before they

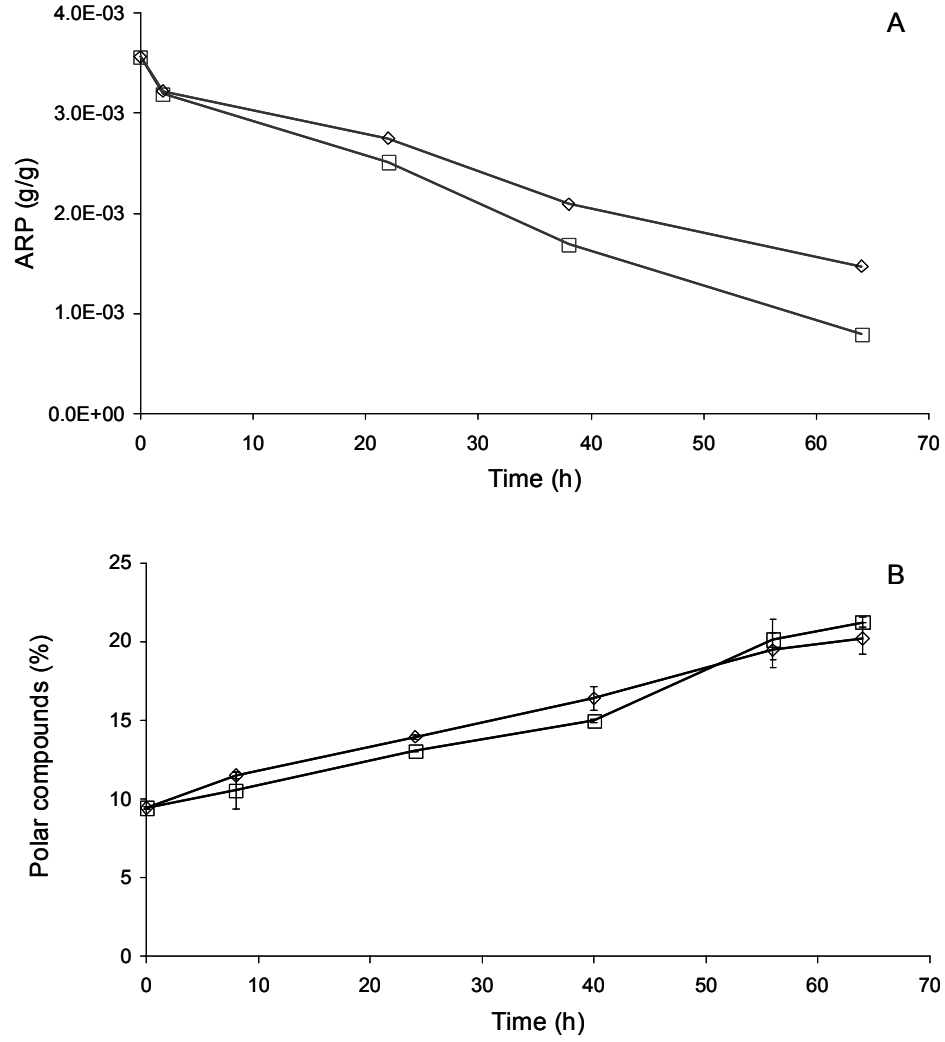
can provide free radicals for further chain reaction propagation.[5] This means that the amount of alkyl radicals at 180 °C would be substantially lower than at 110 °C. When fewer free radicals are present, fewer antioxidants will react, and the ARP will decrease slower. These findings support the theory that a nonradical mechanism is responsible for oil degradation at frying temperature rather than autoxidation.[15]

Several decomposition products are volatiles, such as aldehydes, that contribute to rancidity. Odour detection thresholds for aldehydes resulting from lipid oxidation are low. Hexanal, for example has an odour threshold in oil of 0.3 mg/kg.[16] This suggests that assessors may perceive rancidity in oil already after a low level of oxidation. Once oil was perceived as rancid, the assessors could not distinguish between different levels of rancidity. For frying oil the rancidity of the samples after 0 and 8 h was significantly different from the other points, and for soybean oil only the 0 h sample was significantly different. This may be explained by the fact that soybean oil has quite a strong odour from itself, whereas frying oil has a neutral odour. In oil with a neutral odour it may be easier to smell differences in rancidity. Similar results were obtained with olive oil heated for 22 h at 100 °C.[17] Once the oil was rancid (after 9 h), both the flavour description and flavour score did not change in the remaining time of the experiment.

The ARP of frying oil decreased faster than that of soybean oil. This was not expected, because soybean contains more PUFAs, which are very sensitive for oxidative degradation.[2] On the other hand, Pellegrini *et al*.[18] found that the antioxidative activity of soybean oil was the highest amongst several other vegetable oils. Also, Valavanidis *et al*.[10] showed that the ARP of soybean oil decreased less after heating for 2 h at frying temperature than other vegetable oils. Soybean oil is known to be rich in γ- and δ-tocopherol, which exhibit a strong antioxidative effect in food systems.[19] The starting value of the ARP of soybean oil was also higher than that of frying oil. Moreover, γ- and δ-tocopherol possess a high thermostability.[20] The difference in ARP decrease between frying oil and soybean oil may, therefore, be explained by the difference in amount and thermostability of the antioxidants present in the oils.

Oil deterioration by solely heating and heating with intermediate frying of French fries

The results of the analyses of oil samples after heating at 180 °C and after heating with intermediate frying of French fries are given in Figure 7.3.



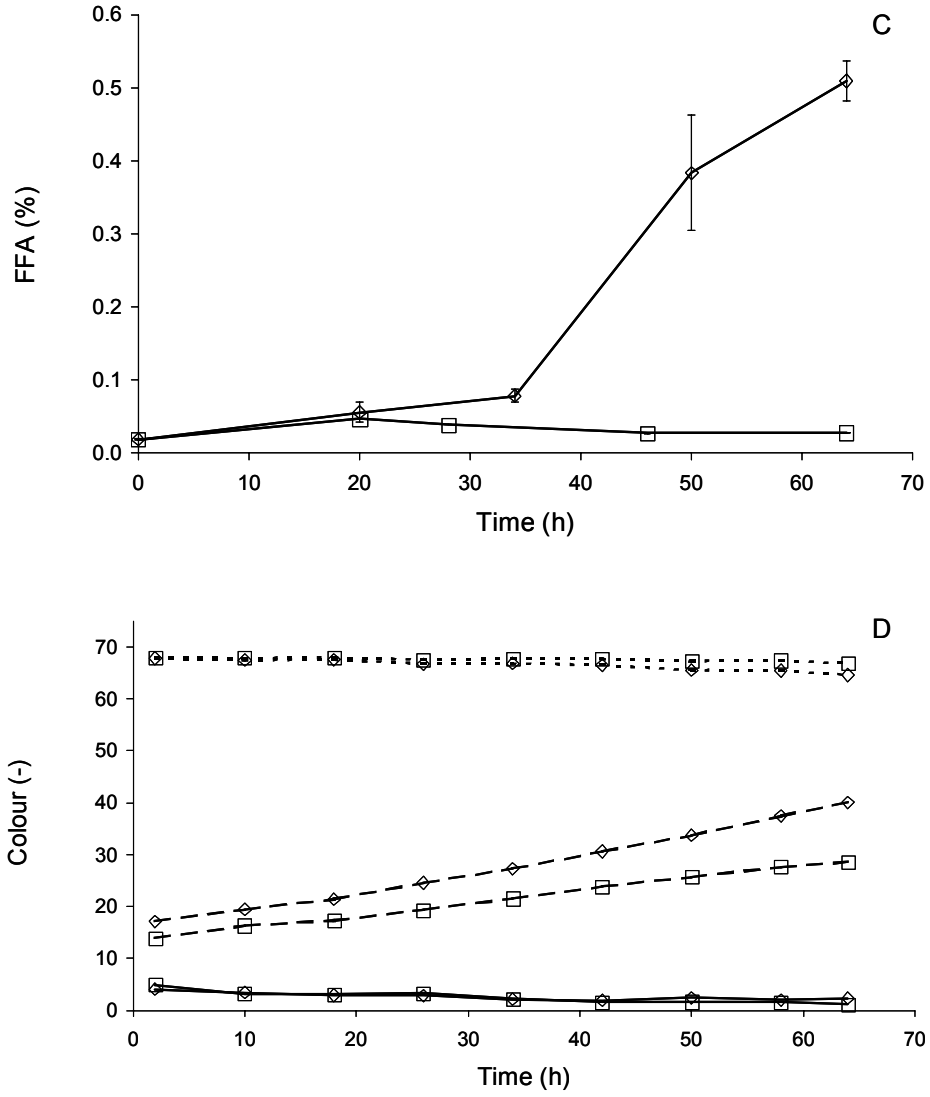


Figure 7.3. ARP (A), polar compounds (B), FFA (C), and colour (D) of frying oil after heating at 180 °C (□) and after heating with intermediate frying of French fries every hour (◊). Colour measurements are expressed in L (- - -), a (——), and b (– –).

The curve of the ARP of oil samples that were solely heated (Figure 7.3A) is similar to Figure 2B, in which the oil had the same treatment. The ARP of oil with intermediate frying decreased significantly slower than oil that was solely heated. FFA values (Figure 7.3C) were significantly higher for oil samples with intermediate frying of French fries. This can be explained by the fact that water, in the form of steam, was released from the product during frying. A steam blanket covered the oil, so that the oxygen supply was limited,[21] but the contact of steam with oil induced hydrolysis. The increase of polar compounds (Figure 7.3B) did, however, not differ significantly between the two situations. The amount of polar compounds is generally regarded as a good measure for overall oil quality.[7,12] Therefore, it seems that the overall oil quality is equal for both situations, but frying of French fries results in a higher degree of hydrolysis, whereas solely heating results in more oxidation.

Another explanation for a higher ARP with intermediate frying may be that compounds with antioxidative properties migrated from the French fries to the oil during frying. In Figure 7.3D it is shown that the colour of both oils became darker by the decrease of L*-values and more yellow by the increase of b*-values. The colour change may be caused by thermal and oxidative reactions such as polymerisation that occur at high temperature. The colour of the oil in which French fries were fried changed, however, significantly faster than the oil that was solely heated. This can be explained by the formation of Maillard reaction products during frying.[22] These compounds, but also other compounds present in potato such as chlorogenic acid, are known to have antioxidative properties.[23]

7.4 CONCLUSION

At 110 °C the decrease of ARP correlated well with the increase of PV. It was observed that the ARP decreased faster at 110 °C than at 180 °C, suggesting that lipid oxidation is slower at frying temperature due to different mechanisms. Furthermore, it was shown that frying French fries in oil results in a slower decrease of ARP than solely heating the oil suggesting that antioxidative factors were released from French fries. Antiradical power gives insights in early lipid oxidation events at frying conditions rather than hydroperoxides and secondary oxidation products.

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Chapter 8

General discussion

8.1 INTRODUCTION

The aim of this thesis was to develop a fundamentally new process for the production of French fries in order to reduce environmental and energy costs. Pre-drying in hot air and par-frying in oil were replaced by a treatment with superheated steam, and vacuum cooling was used for cooling and freezing. Unfortunately, this new process did not result in French fries of sufficient quality (Chapter 2). The main problem was skin formation on the surface resulting in a tough product with a fatty appearance. Moreover, the layer of oil present on the product surface slowed down the release of flavour compounds (Chapter 5). Due to concessions made to improve the product quality, the final energy reduction was limited. Because of the high investment costs, the new process does not have enough economical perspective.

Nevertheless, the work described in this thesis greatly enlarged the knowledge about processes that occur in French fries on micro-scale, and about the influence of process conditions on several quality aspects. In this chapter the main achievements will be discussed.

8.2 MECHANISM OF SKIN AND CRUST FORMATION

The main obstacle of the new process was skin formation. In Chapter 2 a theory about this phenomenon was proposed based on visual observations during finish-frying, sensory analysis, and information about drying and frying processes in literature.[1-7] During the superheated steam treatment water evaporates from the product surface. In the beginning this is free water, but later in the process the surface starts to dry out. Water is transported from the core to the surface because of a concentration gradient. If evaporation of water from the surface is higher than transport from the core to the surface, the outer cell layers will dry out and a skin will be formed. During subsequent finish-frying in oil the water transport is hindered, causing pressure to build up in the product until the skin breaks at the weakest point. After finish-frying oil cannot enter the crust, resulting in a fatty appearance. During conventional par-frying in oil, water vapour is formed under the surface pushing cells apart and in this way creating a porous crust. The water transport is not hindered during finish-frying, and oil can enter the crust after frying. This theory was confirmed using Confocal Scanning Laser Microscopy. In Chapter 3 it was shown that skin

formation occurred with excessive pre-drying in hot air as well. Textural changes, caused by superheated steam and hot air, were very similar. Only two or three dried out cell layers were enough to hinder moisture and oil transport during and after frying. The main difference between a skin and a crust was that a crust consisted of a porous structure with open space between the cells, whereas a skin consisted of a compact structure with no open space. It seems that if no water is present between cells after pre-drying, there is no driving force to separate individual cells during frying. The multiple cell layers will be separated as a whole from the surface during frying forming blisters. Furthermore, excessive drying resulted in reduced crispness. In Chapter 3 a linear correlation between crispness and the number of peaks in the force-deformation curve was found. This suggests that perceived crispness is closely related to the breaking events that occur when the surface of a French fry is penetrated. Crispy products, which have separate cells in the crust area, yield more breaking events, and thus more peaks in the force-deformation curve than products with a compact surface structure, in which several cells exist in one layer.

A longer frying time at constant frying temperature, or a higher frying temperature at constant frying time will increase the crispness of French fries. Drying prior to frying will also result in a crispier product. It is, however, the question whether the enhanced crispness can be attributed to the process parameters, or that it is a result of the difference in moisture content after frying. Moisture content is an important aspect for the observed crispness, and lower moisture content generally results in a crispier product.[8] In Chapter 3 an experimental design was used to study the effect of pre-drying and par-frying temperature on the crispness of French fries independent from the moisture content. This was done by adjusting the frying time in such a way that all samples had equal final moisture contents. This approach showed that a par-frying temperature of 180 °C improved crispness, but no linear correlation between par-frying temperature and crispness was found. Longer pre-drying did not result in increased crispness. On the contrary, pre-drying until 20% weight loss caused blister formation, which reduced crispness.

8.3 FRENCH FRIES FLAVOUR

Flavour is an important quality aspect of French fries. In Chapter 4 compounds responsible for French fries flavour were identified, and in Chapter 5 the release of some of these compounds was followed. Salt addition was shown to accelerate the release of flavour compounds. This salting-out effect may contribute to enhancement of flavour generally perceived after addition of salt. Longer frying times resulted in an increased amount of released flavour in the nose space. After a standard finish-frying time of 4 min already 85% of the amount of flavour is formed in the Maillard reaction. This suggests that some acrylamide formation in French fries cannot be avoided, as acrylamide is formed in the Maillard reaction as well. About 15% of the amount of flavour originated from lipid degradation. In Chapter 7 it was shown that assessors observe rancidity of frying oil already after a short frying time. Volatile compounds observed in frying oil are also observed in the fried product.[9] This suggests that some rancidity is not necessarily negative, as volatiles from lipid oxidation contribute to the fried note of French fries.

8.4 ACRYLAMIDE

Although acrylamide has received a lot of attention the last years, a kinetic model to predict acrylamide formation has not been published so far. The first attempt to develop such a model for a glucose-asparagine reaction system is described in Chapter 6. The model was able to give a reasonable estimation for the formation of acrylamide and melanoidines in an aqueous model system. Acrylamide showed to be an intermediate product in the Maillard reaction. Therefore, prolonged heating at 160–200 °C resulted in breakdown of acrylamide. This suggests that prolonged finish-frying of French fries would also reduce the acrylamide content. In practice this may, however, not be the best solution. Grob *et al*. [10] used professional cooks to prepare French fries and it was shown that acrylamide is formed mainly in the last part of the finish-frying process. At the time French fries have optimal characteristics for consumption, the acrylamide content is still increasing. Prolonged frying may eventually result in a decrease of acrylamide, but the product will most likely be dark, have a bitter off-taste, and have a high oil content. In this perspective, the suggestion that colour is a good predictor for acrylamide formation [11,12] is not completely true, but works as rule of thumb in practice. To keep the acrylamide content of French fries at an acceptable level, manufacturers should select potatoes with low reducing sugar

content and control storage and blanching conditions, while at finish-frying attention should be paid to the temperature (170–175 °C) and the colour. An acrylamide-free product may be possible by applying the enzyme asparaginase. In this way asparagine is degraded selectively, and other amino acids present can contribute to colour and flavour. It is, however, not clear whether colour and flavour are affected, and if this method is economically attractive.

8.5 FUTURE PERSPECTIVES

In Chapter 2 it was shown that replacing the par-frying step with a superheated steam treatment influenced texture and appearance in a negative way. It was stated that a frying step is necessary to produce good quality French fries. The option of using superheated steam instead of finish-frying was, however, not discussed. The desired porous crust structure is created during par-frying in oil, and this may create enough channels for water transport during the finishing step in superheated steam. This suggests a process similar to that of French fries finished in the oven, but superheated steam has distinct advantages compared to hot air. As mentioned in Chapter 2, with superheated steam the product temperature and drying rate can be controlled better than with hot air. Therefore, the process is probably much faster and it is possible to achieve a better product quality than with hot air finishing in an oven. If an acceptable product quality is possible in a short time, superheated steam finishing could be attractive for the finish-frying industry including fast food restaurants and cafeterias. In the current situation oil for finish-frying can only be used for several days, after which it has to be discarded. Using superheated steam for finish-frying instead of oil would obviously reduce costs. The final oil content of the product would decrease as well. If the production process up to finish-frying does not change, the final oil content of standard 10 × 10 mm French fries (5% oil, 68% moisture before finish-frying) would be about 6.1% (at 50% moisture after finish-frying). As the final oil content is currently about 10%, this would be an enormous reduction of almost 40%. Nevertheless, it should be taken into account that a superheated steam facility requires a substantial investment. The product quality and the return on investment remain decisive for industrial application.

Crispness is one of the most important quality aspects of French fries. The industry continually aims to further improve crispness, and to stabilise crispness for a longer time after finish-frying.

In Chapter 3 it was shown that par-frying at 180 °C resulted in a higher crispness than frying at 160–170 °C. It seemed that increasing the temperature difference between the oil and product enhanced crispness. Further increasing the oil temperature, however, is not advisable, because oil deteriorates rapidly above 180 °C and harmful compounds may be formed. Vacuum frying could be an interesting option, because in this way the temperature difference between product and oil is realised by decreasing the product temperature.

French fries are consumed for pleasure, and they are widely settled in the Western diet. However, consumer awareness about health aspects of foods is increasing. Obesity is generally known to increase the risk of coronary heart diseases, diabetes, and certain types of cancer. The health image of French fries is generally low, and recent publications about acrylamide and trans fatty acids in frying oil aggravated the situation. This raises the question: how unhealthy is it to eat French fries? Looking at calories and portion size, it depends where French fries are compared with. As the meal component that delivers carbohydrates, French fries supply more calories than rice and pasta products. However, a portion of French fries supplies fewer calories than many other snack products.[13] Note that the type and amount of sauce consumed with French fries cannot be neglected. Mayonnaise has an oil content of 80%, and other types of emulsion-based snack sauces contain at least 25% of oil. Although the oil content of ketchup is very low, it contains about 24% of sugar. Calories are, however, not the whole story. As already mentioned the amount of oil uptake and acrylamide formation strongly depend on the way of preparation. Also, consumption of oil is not necessarily harmful for health. Saturated and trans fatty acid should be avoided, but unsaturated fatty acids are, in the right amount, even beneficial in preventing coronary heart disease (Chapter 1). Furthermore, the overall consumption pattern and the physical condition are much more important for health than the consumption of individual foodstuffs. In conclusion, French fries do not have to be unhealthy, if attention is paid to the frying time, the frying temperature, the type and age of the oil, and the type and amount of snack sauce added. Therefore, French fries can be incorporated in a balanced diet, and are not necessarily unhealthy.

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Summary

The production process of French fries has grown from the kitchen to a large-scale industry through the years. Problems have been solved on the way and cost reductions have been achieved. In Chapter 1 an introduction about the production process, quality aspects, and research about French fries is given. The current production process, however, still has a number of disadvantages. The energy use in the form of natural gas and electricity is high and costly environmental measures are necessary to reduce the emission of vapours from the fryer. Also, frying oil is a relatively expensive raw material that contributes considerably to the caloric value of the product. The aim of this thesis was to develop a new oil-free process, in which superheated steam (SHS) is used to replace pre-drying and par-frying, and vacuum cooling is used for cooling and freezing. With the new process the energy use can be reduced substantially (natural gas by about 70%, electrical energy by about 50%). No oil is used in the process and this means, besides a cost reduction, that no measures have to be taken against odour nuisance. Finish-frying is, however, still performed in oil.

The development and evaluation of the new process is described in Chapter 2. Many small-scale experiments were carried out with a pilot plant to test the feasibility of the new process. The quality of every batch was determined by sensory analysis and the moisture and fat content were measured. When SHS was used at atmospheric pressure, the product got overdone quickly. To prevent this, a lower pressure was applied. In this way it was possible to obtain a product with desired doneness and moisture content, but this caused skin formation on the French fry surface. A skin resulted in a tough crust and a fatty appearance after finish-frying. With Confocal Scanning Laser Microscopy (CSLM) it was shown that a skin consisted of dried out cell layers in a compact structure, whereas a crispy crust consisted of a porous structure. Vacuum freezing caused skin formation as well. By introducing a frying step in oil, and using conventional cooling and freezing, the product quality became comparable to conventional French fries. The only remaining difference between this final new process and the conventional process was that hot air for pre-drying was replaced by SHS. The resulting energy reduction was, unfortunately, insufficient to justify the required investment for SHS equipment.

In Chapter 3 crust and skin formation were further investigated. An experimental design was used to study the effect of pre-drying (to 10, 15, and 20% weight loss) and par-frying

temperature (160, 170, and 180 °C) on the crispness of French fries. Because moisture content is generally known to influence crispness to a great extent, the par-frying time was adjusted to obtain equal moisture content and internal texture for all samples. Crispness was evaluated with a sensory panel, instrumentally with a Texture Analyser, and microscopically with CSLM. Par-frying at 180 °C resulted in a crispier product than par-frying at 160 and 170 °C. Pre-drying to 20% weight loss lead to blisters and reduced crispness in comparison with pre-drying to 10 and 15% weight loss. CSLM showed that the compact cell structure observed in blisters was similar to the structure in a skin after SHS treatment (Chapter 2). Instrumental texture measurements showed a good correlation with sensory crispness.

The flavour of French fries was studied extensively. In Chapter 4 volatile compounds, released from French fries at mouth conditions by purge-and-trap, were trapped on Tenax TA, and identified with GC-MS. GC-Olfactometry was used to determine odour active compounds with a trained panel using the detection frequency method. A total of 122 compounds could be identified. Based on relative peak areas 85 % originated from sugar degradation and/or Maillard reaction, and 15 % from lipid degradation. About 50 odour active compounds were, due to co-elution, responsible for 41 odours observed by the assessors. They perceived a strong malty and fried potato note, combined with caramel/ buttery, green, spicy, and deep-fried notes. Also chemical and sweaty odours were observed.

Subsequently, in Chapter 5 MS-Nose was used to follow flavour release from French fries using both assessors (*in vivo*) and a mouth model system (*in vitro*). Several volatiles measured with MS-Nose could be identified with MS-MS. The effect of frying time, salt addition, and an alternative process using superheated steam was determined on I_{max} (maximum intensity of compounds) and on t_{max} (time of maximum intensity). *In vitro* a “chewing” frequency of 0.60 Hz caused an increased t_{max} for low molecular compounds. Above 0.93 Hz further increasing the frequency did not affect t_{max}. Trends observed with *in vivo* experiments could be verified with *in vitro* experiments. I_{max} correlated well with frying time. Addition of salt resulted in a decreased t_{max}, suggesting a salting-out effect. The alternative process caused a layer of oil on the surface and this resulted in a higher t_{max}, but no effect on I_{max} was found. This phenomenon may be important for the sensory quality, and would not have been observed with static volatile measurements, demonstrating the value of flavor release measurements.

The Maillard reaction is important for the flavour and colour development, but is responsible for the formation of the carcinogenic compound acrylamide as well. In Chapter 6 the first attempt to

develop a kinetic model for the formation of acrylamide in a glucose-asparagine reaction system is described. Equimolar solutions (0.2 M) of glucose and asparagine were heated at different temperatures (120–200 °C) at pH 6.8. Besides the reactants, acrylamide, fructose, and melanoidines were quantified after predetermined heating times (0–45 min). Multiresponse modelling using non-linear regression with the determinant criterion was used to estimate model parameters. The proposed model resulted in a reasonable estimation for the formation of acrylamide in an aqueous model system, although the behaviour of glucose, fructose, and asparagine was slightly underestimated. The formation of acrylamide reached its maximum at the time the concentration of sugars reached zero. This supports previous research, showing that a carbonyl source is needed for the formation of acrylamide from asparagine. Furthermore, it suggests that acrylamide is an intermediate of the Maillard reaction rather than an end product.

Lipid oxidation is important for the quality of French fries, because it contributes to the flavour and it influences the performance of the frying oil. In Chapter 7 early lipid oxidation events were studied at frying conditions by following antiradical power (ARP). The 2,2-diphenyl-1-picrylhydrazyl radical (DPPH•) test was used to determine the ARP. As oil does not dissolve completely in methanol, which is generally used for the DPPH• test, butanol was used instead. Changing the solvent did not influence the value of the ARP. The decrease of the ARP correlated well with the increase of the peroxide value for soybean oil heated at 110 °C. Sensory analysis showed that rancidity of soybean oil and frying oil, heated at 180 °C, was perceived at an earlier stage than the ARP decreased. Once the oil was perceived as rancid, the intensity of rancidity did not change significantly upon further heating. The ARP of soybean oil was found to decrease faster at 110 °C than at 180 °C, suggesting different mechanisms of radical formation. The total polar compounds of frying oil, in which French fries were fried, did not differ significantly from frying oil that was solely heated. However, frying of French fries caused more hydrolysis of the oil, while the ARP decreased faster when the oil was solely heated. This suggests that compounds with antioxidative properties migrated from the product to the frying oil.

Chapter 8 contains the main achievements and general discussion. The mechanism of crust formation is discussed and suggestions for further improvement of crispness are proposed. The formation of acrylamide is discussed in relation to colour and flavour. Finally, some future perspectives are given including the possibility of using SHS for finish-frying and health aspects of French fries.

Samenvatting

Het productieproces van frites is in de loop der jaren vanuit de keuken gegroeid naar een grootschalige industrie. Voorkomende problemen zijn stuk voor stuk opgelost en besparingen zijn op onderdelen gerealiseerd. In Hoofdstuk 1 wordt een overzicht van het productieproces, kwaliteitsaspecten en onderzoek aan frites gegeven. Het huidige proces heeft nog steeds een aantal nadelen. Het energiegebruik in de vorm van gas en elektra is hoog en er zijn kostbare milieumaatregelen nodig om emissies en geuroverlast te reduceren. Bovendien is frituurolie een relatief dure grondstof, die aanzienlijk bijdraagt aan de calorische waarde van het product. Het doel van het onderzoek was om een nieuw, olievrij proces te ontwikkelen waarbij oververhitte stoom (SHS) wordt gebruikt voor voordrogen en voorbakken en waarbij koelen en vriezen plaatsvinden door vacumeren. Met het nieuwe proces kan het energiegebruik sterk worden teruggebracht (gas ca. 70%, elektra ca. 50%). Er wordt in het proces geen olie gebruikt en dat betekent, naast een kostenbesparing, dat er geen maatregelen nodig zijn tegen geuroverlast. Het afbakken vindt nog wel in olie plaats.

De ontwikkeling en evaluatie van het nieuwe proces wordt in Hoofdstuk 2 beschreven. Om de haalbaarheid van het nieuwe proces te testen zijn een groot aantal kleinschalige experimenten uitgevoerd met een stoompilot. De kwaliteit van elke batch is bepaald met sensorische analyse en tevens zijn het vocht- en vetgehalte bepaald. Het gebruik van SHS bij atmosferische druk leidde snel tot een te gaar product. Om dit te voorkomen werd een lagere druk toegepast. Op deze manier was het mogelijk om een product te maken met de gewenste gaarheid en vochtgehalte. Er ontstond echter een huid op het fritesoppervlak, die na afbakken resulteerde in een taaie korst met een laagje olie op het oppervlak. Confocale Scanning Laser Microscopie (CSLM) maakte zichtbaar dat de huid bestond uit uitgedroogde cellagen in een compacte structuur, terwijl een poreuze structuur leidde tot een krokante korst. Vacumeren bleek eveneens huidvorming te veroorzaken. Om dit te voorkomen werd een voorbakstap in olie geïntroduceerd en werd er conventioneel gekoeld en ingevroren. De productkwaliteit werd daardoor vergelijkbaar met conventionele frites. Het enige resterende verschil met het conventionele proces was dat bij voordrogen hete lucht werd vervangen door SHS. Helaas was de resulterende energiebesparing onvoldoende om de vereiste investering in SHS apparatuur te rechtvaardigen.

In Hoofdstuk 3 zijn huid- en korstvorming nader bestudeerd. Een "experimental design" is gebruikt om het effect te bepalen van voordrogen (tot 10, 15 en 20% gewichtsafname) en voorbaktemperatuur (160, 170, and 180 °C) op de krokantheid van frites. Omdat bekend is dat krokantheid sterk wordt beïnvloed door het vochtgehalte, is de voorbaktijd zo aangepast dat alle monsters hetzelfde eindvochtgehalte en dezelfde gaarheid hadden. De krokantheid is bepaald met een sensorisch panel, met een Texture Analyser en met CSLM. Voorbakken bij 180 °C resulteerde in een krokanter product dan voorbakken bij 160 en 170 °C. Voordrogen tot 20% gewichtsafname leidde tot blaasjes op de korst en een verminderde krokantheid in vergelijking met voordrogen tot 10 en 15% gewichtsafname. Met CSLM bleek dat de compacte celstructuur in blazen vergelijkbaar was met die van huidvorming door SHS (Hoofdstuk 2). Instrumentele textuurmetingen vertoonden een goede correlatie met sensorische krokantheid.

Het aroma van frites is uitgebreid onderzocht. In Hoofdstuk 4 werden vluchtige verbindingen met "purge-and-trap" geëxtraheerd uit frites onder mondomstandigheden, geabsorbeerd op Tenax TA en vervolgens geïdentificeerd met GC-MS. GC-Olfactometrie werd gebruikt om met een getraind panel geuractieve componenten te bepalen volgens de "detection frequency method". In totaal werden 122 componenten geïdentificeerd. Hiervan was, op basis van de relatieve piekoppervlakte, 85% afkomstig van suikerafbraak en/of de Maillard-reactie en 15% van vetoxidatie. Ongeveer 50 geuractieve componenten waren door coëlutie verantwoordelijk voor 41 door de panelleden waargenomen geuren. Ze constateerden een sterke moutachtige en gefrituurde aardappelgeur, gecombineerd met karamel/boterachtige, groene, gebakken en kruidige accenten. Bovendien werden bepaalde geuren omschreven als chemisch en zweetlucht.

Vervolgens is in Hoofdstuk 5 het vrijkomen van geuractieve componenten uit frites gevolgd met zowel panelleden (*in vivo*) als met een mondmodelsysteem (*in vitro*). Verscheidene vluchtige verbindingen, die werden gedetecteerd met MS-Nose, konden worden geïdentificeerd met MS-MS. Het effect van afbaktijd, zout en het nieuwe proces met SHS is bepaald op de maximale intensiteit (I_{max}) en het tijdstip van maximale intensiteit (t_{max}) van de componenten. *In vitro* bleek een "kauwfrequentie" van 0,60 Hz bij laagmoleculaire componenten te zorgen voor een toename van t_{max}. Verdere verhoging van de frequentie boven 0,93 Hz had echter geen invloed op t_{max}. Trends, die werden gevonden bij *in vivo* experimenten, werden bevestigd met *in vitro* experimenten. Er was een lineaire correlatie tussen baktijd en I_{max}. Toevoegen van zout verlaagde t_{max} en dit suggereert een uitzouteffect. Het nieuwe proces veroorzaakte een laagje olie op het oppervlak en dit verhoogde t_{max}, maar er werd geen effect op I_{max} gevonden. Dit

fenomeen zou van belang kunnen zijn voor de sensorische kwaliteit. Met alleen statische meetmethoden zou het effect niet zijn waargenomen, waarmee het belang van deze analysemethode aangetoond wordt.

De Maillard-reactie is belangrijk voor de ontwikkeling van kleur en aroma, maar is ook verantwoordelijk voor het ontstaan van het carcinogene acrylamide. In Hoofdstuk 6 wordt een eerste poging beschreven een kinetisch model te ontwikkelen voor de vorming van acrylamide in een reactiesysteem van glucose en asparagine. Een equimolaire oplossing (0.2 M) van glucose en asparagine is bij pH 6.8 bij verschillende temperaturen (120–200 °C) verhit. Het verloop van de reactanten, acrylamide, fructose en melanoidines werd gekwantificeerd en gevolgd in de tijd (0–45 min). Om de modelparameters te schatten is gebruik gemaakt van multiresponse modelleren via non-lineaire regressie met het determinantcriterium. Het model was redelijk in staat de vorming van acrylamide te voorspellen, hoewel het gedrag van glucose, fructose en asparagine enigszins werd onderschat. De vorming van acrylamide bleef toenemen zolang er suiker aanwezig was. Dit ondersteunt eerder onderzoek waarin werd aangetoond dat een carbonylgroep nodig is voor de vorming van acrylamide uit asparagine. Bovendien suggereert dit dat acrylamide een intermediair van de Maillard-reactie is in plaats van een eindproduct.

Vetoxidatie is belangrijk voor de kwaliteit van frites, omdat het bijdraagt aan het aroma en omdat het de bakkwaliteit van de olie beïnvloedt. In Hoofdstuk 7 wordt vroege vetoxidatie beschreven onder frituuromstandigheden door de antioxidatieve capaciteit (ARP) te volgen. De ARP is bepaald met de 2,2-diphenyl-1-picrylhydrazylradicaal (DPPH•)-test. Olie werd opgelost in butanol, omdat olie niet geheel oplosbaar is in methanol, dat normaal wordt gebruikt voor de DPPH•-test. Het veranderen van oplosmiddel bleek geen invloed te hebben op de ARP. De afname van de ARP correleerde goed met de toename van het peroxidegetal voor sojaolie, verhit bij 110 °C. De ransheid van sojaolie en frituurolie werd bij 180 °C eerder door de panelleden waargenomen dan dat de ARP afnam. Als de olie eenmaal rans werd bevonden dan veranderde de mate van de ransheid niet door verder te verhitten. De ARP van sojaolie nam bij 110 °C sneller af dan bij 180 °C en dit suggereert een verschillend mechanisme voor radicaalvorming. Het gehalte aan totale polaire componenten van frituurolie waarin frites werd gebakken verschilde niet van frituurolie die alleen werd verhit. Bij alleen verhitten nam de ARP sneller af, terwijl bij frituren meer hydrolyse van de olie optrad. Dit suggereert dat componenten met antioxidatieve eigenschappen vanuit het product naar de olie zijn gemigreerd.

Hoofdstuk 8 bevat de belangrijkste conclusies van het onderzoek en een algemene discussie. Het mechanisme van korstvorming wordt toegelicht en er worden suggesties gegeven om de krokantheid van frites verder het verbeteren. Tevens wordt de relatie tussen de vorming van acrylamide en de ontwikkeling van kleur en aroma besproken. Ten slotte wordt een toekomstperspectief gegeven waarin wordt ingegaan op de mogelijkheid van het gebruik van SHS bij afbakken en gezondheidsaspecten van frites.

Nawoord

“Promoveren op frites, kan dat dan?” Deze vraag, meestal gepaard met een gefronste blik, kreeg ik de afgelopen 4 jaar regelmatig te horen. Nou, beste mensen, het kan dus. Niet dat het altijd even soepel gegaan is hoor, integendeel. Zoals in Hoofdstuk 2 te lezen is, waren er nogal wat problemen met de productkwaliteit en bleef er uiteindelijk niet veel van het oorspronkelijke idee over. Dit was natuurlijk jammer voor het onderzoek, maar het betekende ook dat de financiering voortijdig ophield. Daarom ben ik zeer erkentelijk dat Aviko mijn voorstel voor een aanvullend onderzoek naar krokantheid van frites honoreerde en dat ik bovendien een groot deel van de resultaten mocht publiceren. In dit kader wil ik ook NIZO food research en WCFS bedanken voor de meettijd die me gegund werd.

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Wil

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WAM van Loon, JPH Linssen, AEM Boelrijk, MJM Burgering, AGJ Voragen. Real-time flavor release from French fries using MS-Nose (submitted).

WAM van Loon, JE Visser, JPH Linssen, DJ Somsen, HJ Klok, AGJ Voragen. Effect of pre-drying and par-frying conditions on the crispness of French fries (submitted).

Curriculum vitae

Wilhelmus Antonius Maria (Wil) van Loon werd geboren op 5 mei 1976 te Veldhoven. In 1994 behaalde hij het diploma Atheneum aan het Anton van Duinkerken College te Veldhoven. In datzelfde jaar startte hij met de studie Levensmiddelentechnologie aan HAS Den Bosch. Tijdens deze opleiding liep hij stage bij Delicia BV te Tilburg en Quest International te Naarden en deed hij een afstudeerproject in opdracht van Benier Nederland BV te 's-Hertogenbosch. Hij behaalde het ingenieursdiploma (BSc) in juli 1998 met specialisaties in Productontwikkeling en Bakkerijtechnologie. Aansluitend studeerde hij Levensmiddelentechnologie aan Wageningen Universiteit. Hij deed afstudeervakken bij Levensmiddelenchemie en Levensmiddelen-microbiologie en behaalde het ingenieursdiploma (MSc) in september 2000. Van oktober 2000 tot april 2001 werkte hij als projectmedewerker bij TNO-MEP te Apeldoorn. In mei 2001 startte hij als AIO bij de leerstoelgroep Levensmiddelenchemie aan het promotieonderzoek dat in dit proefschrift staat beschreven. Sinds april 2005 is hij werkzaam als Sensory Researcher bij Friesland Foods te Deventer.

Overview of completed training activities

Discipline specific activities

Courses

Practical capillary gas chromatography, Interscience, Breda (2001)

Advanced Food Analysis, VLAG, Wageningen (2002)

Applied Statistics, dr. W. Hammers, Wageningen (2002-2003)

Full-automatic thermal desorption, Interscience, Breda (2004)

Meetings

Symposium "Know what you eat", Nicolas Appert, Wageningen (2002)

Symposium "Chemistry, flavor and texture of lipid-containing foods", American Chemical Society, New York (2003)

Scientific Exchange, Hamburg University, Germany (2004)

5th International Potato Processing Convention, Amsterdam (2004)

General courses

PhD student week VLAG (2001)

Organising and supervising thesis projects, Wageningen University (2001)

Writing and presenting a scientific paper, Mansholt Institute, Wageningen (2002)

Food Chemistry PhD trip USA (2002)

Introduction Marketing and Management, Wageningen University (2003)

Food Chemistry PhD trip, Japan (2004)

Optionals

Preparation PhD research proposal

Food Chemistry Seminars, Wageningen University (2001-2005)

Food Chemistry Colloquia, Wageningen University (2001-2005)

EET project meetings

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