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Investigations of meat stock

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Publication date:
2010

Document Version
Peer reviewed version

Citation for published version (APA):
Snitkjær, P. (2010). Investigations of meat stock: from a molecular gastronomy perspective. Department of Food Science, University of Copenhagen.



**Investigations of meat stock
from a Molecular Gastronomy perspective**

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November 2010**

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PREFACE

The present thesis presents the work of my PhD at the Department of Food Science, University of Copenhagen, Denmark from February 2006 to November 2010. The PhD has been the first conducted within the field of *Molecular Gastronomy* at the University of Copenhagen, thus one of the objectives of the PhD has been to define the scientific field and implement it into teaching at the University.

The work has been supervised by Professor Leif H. Skibsted, Ass. Professor Michael B. Frøst and Ass. Professor Jens Risbo. I would like to thank my supervisors for inspiration and guidance throughout the project. At the Department of Food Science I would further like to thank Karsten Olsen for his support in all practical matters, Louise M. Mortensen for valuable discussions and feedback on the thesis, and Michael Agerlin for advice on the gas chromatographic analysis. I would further like to thank Professor Peter Barham, University of Bristol and affiliated Professor at the University of Copenhagen for valuable discussions and especially for his initiative and great effort in completing the review on *Molecular Gastronomy* (Paper II).

Experiments related to Paper IV were carried out at Department of Viticulture and Enology, University of California, Davis in spring 2007 and November 2008, supervised by Professor Susan Ebeler and Professor Hildegard Heymann. I would like to thank Prof. Ebeler and Prof. Heymann for their supervision and for hosting me during my two stays in California. I would further like to thank Kevin Scott at the Department for great support in all practicalities.

Finally, thanks to Nicholas Bailey for proofreading the thesis.

November 2010

Pia Snitkjær Bailey

ABSTRACT

Molecular Gastronomy is an emerging scientific discipline which is concerned with all culinary transformations and other matters relevant to obtaining high quality foods and meals. Meat stock preparation is an example of a common kitchen process that has received little attention by scientists but a lot of attention by chefs. Understanding the chemistry and physics of this basic kitchen procedure is within the scope of Molecular Gastronomy. Meat stock preparation, in particular the *reduction* (boiling down) of meat stocks, forms the basis of this PhD thesis. The thesis contains two parts, of which the first is concerned with the new scientific discipline, Molecular Gastronomy, while the second is a study on meat stock preparation.

Part one contains an elaboration on the aims and scientific core of Molecular Gastronomy. It begins with some background information explaining how the field has evolved and how it relates to traditional food science. It further goes into details with the content of the field and common misconceptions as well as the scope and relevance for society. Finally relevant literature in the field of Molecular Gastronomy is presented, including Paper I (*Scandinavian 'sushi': The raw story*) which exemplifies how development in traditional food science is related to our food culture and preferences. This is done by studying traditional techniques for preserving fish in Scandinavia and how the associated changes in flavour and texture of the fish have formed the basis for how we prepare and appreciate fish today. In addition Paper II (Molecular gastronomy, a new emerging scientific discipline) is presented, which is a comprehensive review of literature in the field.

Part two contains an investigation of flavour formation and preparation techniques when preparing a reduced meat stock. Meat stocks are very important in the traditional French kitchen. They are used as a base in a large range of brown sauces but are also used in for example soups and stews. This part presents the preparation of meat stocks and the related cookbook prescriptions. Some of the identified problems regarding the last step, the reduction (boiling down) of meat stock, are studied in Paper III (*Flavour development during beef stock reduction*). Paper IV (*Beef stock reduction with red wine, effects of preparation method and wine characteristics*) further studies flavour development in meat stock reduction with red wine, and looks into the choice of wine and reduction method. Both studies use a descriptive sensory analysis (perceived flavour) and gas chromatography (volatile compounds) as the main analytical techniques.

The results from Paper III show how the perceived flavours as well as the volatile concentrations change with reduction time. The theory regarding meat flavour formation and volatility of aroma compounds is discussed in relation to the results. The study further shows that the concentration factor, as often referred to by chefs, does not by itself determine the flavour of the reduced stock. The reduction time on the other hand, as often not prescribed, has a large impact on the flavour. The paper further discusses how the flavour of reduced stocks can be controlled to some extent by controlling the rate of water evaporation as given by the relation between reduction time and concentration factor.

Results from Paper IV show how the initial composition of the wine influences the flavour of the reduced red wine stock. It is shown that many initial volatile compounds of the wines are lost whereas the non-volatile compounds are concentrated. Hence the non-volatiles are concluded to have a considerable impact on the flavour after reduction, not least since they are assumed to be precursors to the new aromas formed upon heating. Based on these results it is recommended to choose a red wine for cooking based on its non-volatile composition as expressed in its taste and mouthfeel (astringency, sourness, sweetness and bitterness). Two

different reduction methods, reducing wine and stock *together* versus *separately*, were also shown to have a considerable impact on flavour. The results suggest that precipitation of phenolics and proteins take place if the wine and meat stock are heated together and that this may further reduce the astringency.

The results obtained in the studies on stock reduction provide new insight into the science behind preparation of reduced meat stocks, including the influence of preparation method. The problems investigated have a general character meaning they give fundamental insight into how flavours develop upon cooking in an open pot and which factors are important to control. The work further provides a general insight into the scientific problems related to meat stock preparation and suggestions for further investigations in the field.

RESUMÉ

Molekylær Gastronomi er en videnskabelig disciplin under udvikling der omhandler alle kulinariske processer og andre relevante emner i forbindelse med at opnå mad og måltider af høj kvalitet. Tilberedning af kødfond er et eksempel på en almindelig køkken proces som har fået meget lidt opmærksomhed fra forskere men stor opmærksomhed fra kokke. Forståelse af kemien og fysikken bag denne basis køkken proces ligger indenfor formålet med *Molekylær Gastronomi*. Tilberedning af kødfond, herunder specielt *reduktionen* (indkogningen) af fonderne, er hovedtemaet i denne PhD afhandling. Afhandlingen indeholder to dele, hvoraf den første omhandler den nye videnskabelige disciplin, Molekylær gastronomi, og den anden omhandler tilberedning af kødfond.

Del et uddyber indholdet og formålet med Molekylær Gastronomi. Den starter med baggrundsinformation som forklarer hvordan den videnskabelige disciplin har udviklet sig og hvordan den relaterer sig til traditionel fødevidenskab. Derefter går der mere i detaljer mht. hvad Molekylær Gastronomi dækker over, typiske misforståelser samt formål og relevans for samfundet. Til sidst præsenteres relevant litteratur indenfor emnet, hvilket inkluderer Artikel I (*Scandinavian 'sushi': The raw story*), som eksemplificerer hvordan udviklingen indenfor traditionel fødevidenskab er relateret til vores madkultur og præferencer. Dette er gjort gennem et studie af traditionelle konserveringsteknikker for fisk i Skandinavien og hvordan de associerede ændringer i smag og tekstur af fisken har dannet basis for hvordan vi tilbereder og nyder fisk i dag. I tillæg er Artikel II (*Molecular Gastronomy, a new emerging scientific discipline*) præsenteret, hvilket er en fyldestgørende redegørelse af litteraturen indenfor feltet.

Del to indbefatter et studie af smagsudvikling og tilberedningsteknik ved tilberedning af en reduceret kødfond. Kødfonder er meget vigtige i det traditionelle franske køkken. De bliver anvendt som base i en lang række af brune sovser men bliver også anvendt i for eksempel supper og sammenkogte retter. Del to beskriver tilberedning af kødfonder og de relaterede kokebogsforskrifter. Nogle af de identificerede problemer relateret til den sidste del af tilberedningen, reduktionen (indkogningen), af kødfond undersøges i Artikel III (*Flavour development during beef stock reduction*). Artikel IV (*Beef stock reduction with red wine, effects of preparation method and wine characteristics*) videre undersøger smagsudviklingen i reducerede kødfonder med rødvin, og giver et indblik i betydningen af valg af vin og fremgangsmåde. Begge studier anvender en deskriptiv sensorisk analyse (smagsopfattelsen) og gas kromatografi (flygtige aromakomponenter) som de primære analytiske teknikker.

Resultaterne fra Artikel III viser hvordan den opfattede smag samt koncentrationen af de flygtige forbindelser ændres med reduktionstiden. Teorien omhandlende dannelse af kødsmag og flygtighed af aromakomponenter er diskuteret i relation til resultaterne. Studiet viser yderligere at koncentrationsfaktoren, som der ofte refereres til i kokebøger, ikke i sig selv er afgørende for smagen i den reducerede fond. Reduktionstiden derimod, som ofte ikke foreskrives, har en stor betydning for smagen. Artiklen videre diskuterer hvordan smagen i reducerede fonder kan kontrolleres til en hvis grad ved at kontrollere afdampningshastigheden som er givet af forholdet mellem reduktionstid og koncentrationsfaktor.

Resultater fra Artikel IV viser hvordan den oprindelige komposition af vinen har indflydelse på smagen af den reducerede rødvinfond. Det vises at mange af de flygtige forbindelser i vinen mistes hvorimod de ikke-flygtige komponenter bliver opkoncentreret. Derfor konkluderes det at de ikke-flygtige forbindelser har en

betydelig indflydelse på smagen efter reduktionen, ikke mindst fordi disse antages at være forstadier til aromakomponenter dannet under opvarmning. Baseret på disse resultater anbefales det at vælge rødvin til madlavning (opvarmning) ud fra indholdet af vinens komposition af ikke-flygtige forbindelser som udtrykkes i vinens smag og mundfølelse (astringerende, surhed, sødme og bitterhed). To forskellige reduktionsmetoder, reduktion af vin og fond *sammen* kontra *separat*, var yderligere fundet at have en betydelig indflydelse på smagen af de reducerede fonder. Resultaterne antyder at udfældning af phenoler og proteiner finder sted hvis vin og kødfond opvarmes sammen og at dette yderligere reducerer den astringerende mundfølelse

De opnåede resultater i disse studier giver ny indsigt i videnskaben bag tilberedning af reducerede kødfonder, herunder indflydelse af tilberedningsmetode. De undersøgte problemer har en generel karakter dvs. de giver fundamental indsigt i smagsudvikling under madlavning (opvarmning) i en åben gryde og hvilke faktorer der er vigtige at kontrollere. Projektet giver yderligere en generel indsigt i de videnskabelige problemer relateret til tilberedning af kødfond og forslag til yderligere undersøgelser indenfor dette emne.

LIST OF PUBLICATIONS

Paper I: *Scandinavian ‘sushi’: The raw story* by P. Snitkjær and L.M. Mortensen. Accepted by editors for publication in *The Kitchen as a laboratory: reflections on science inspired by the kitchen*, edited by C. Vega, J. Ubbink and E. van der Linden. The book has been submitted to Columbia University Press, New York, July 2010

Paper II: *Molecular Gastronomy, a new emerging scientific discipline* by P. Barham, L.H. Skibsted, W.L.P. Bredie, M.B. Frøst, P. Møller, J. Risbo, P. Snitkjær and L.M. Mortensen. *Chemical Reviews* 2010, 110 (4), pp 2313-2365.

Paper III: *Flavour development during beef stock reduction* by P. Snitkjær, M.B. Frøst, L.H. Skibsted and J. Risbo. *Food Chemistry*, 2010, 122 (3), pp 645-655.

Paper IV: *Beef stock reduction with red wine, effects of reduction method and wine characteristics* by P. Snitkjær, J. Risbo, L.H. Skibsted, S. Ebeler, H. Heymann, K. Harmon and M.B. Frøst, Accepted for publication in *Food Chemistry* on October 22, 2010.

ABBREVIATIONS

ANOVA	Analysis of Variance
BSc	Bachelor of Science
CDS	Complex Disperse System formalism
CF	Concentration Factor
CSF	Culinary Succes Factors
Experiment P	Power experiment (Paper III)
Experiment T	Time experiment (Paper III)
GC	Gas Chromatography
GMP	Guanosine monophosphate
HPLC	High Performance Liquid Chromatography
IMP	Inosine monophosphate
MG	Molecular Gastronomy
MS	Mass Spectrometer
MSc	Master of Science
MSG	Monosodium Glutamate
NPOS	Non Periodical Organizational Space formalism
PCA	Principal Component Analysis
PC	Principal Component
PLS	Partial Least Square regression
SPME	Solid Phase Micro Extraction

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1 INTRODUCTION

Exploration of cooking and the experience of a meal is a new scientific discipline, called Molecular Gastronomy (MG). MG can be considered a sub-field of Food Science, aiming at understanding culinary transformation in the restaurant or home kitchen and the experience of a good meal in contrast to traditional food science which deals mainly with large-scale production, industrial processes, food safety etc. At the Department of Food Science, University of Copenhagen, MG has existed as a field of research and teaching since 2006. The present thesis aims to describe the essence of the scientific discipline, Molecular Gastronomy, and further to study one particular topic in this field, meat stock preparation.

Part one of the thesis will elaborate on the scientific core of MG, counting also the challenges, aims and relevance for society of further scientific work in the field. Examples of relevant literature will be presented, these include in particular Paper I (*Scandinavian 'sushi': The raw story*) and Paper II (*Molecular gastronomy: a new emerging scientific discipline*) which is a review of the field.

Part two of the thesis is built up around a study of meat stock preparation. Preparation of meat stock is a basic process in the traditional French kitchen which has set the standards for fine dining in most parts of the Western world. Stocks are the basic component in many sauces but have a wide range of applications and thus stock is among the most basic preparations found in any professional kitchen. In French stocks are referred to as 'fonds de cuisine' (foundations of cooking) (The Culinary Institute of America 2006). Meat stocks are often boiled down in order to enhance their flavour and consistency. The decrease in volume by simmering or boiling is referred to as 'reduction' (Larousse 1997; Peterson 2008). The experimental work included in part two of the thesis comprises two studies which focus on the reduction of meat stocks. Paper III (*Flavour development during beef stock reduction*) studies the flavour development through a traditional reduction process while Paper IV (*Beef stock reduction with red wine, effects of preparation method and wine characteristics*) studies the use of red wine in meat stock reductions.

2 MOLECULAR GASTRONOMY, AN INTRODUCTION

Molecular Gastronomy (MG) focuses on the science of cooking or more generally the science behind a good meal. This involves scientific investigation of preparation techniques as well as the study of cultural and social factors affecting diner's perception of the meal. Chapter 3 describes the story of the term Molecular Gastronomy and the key people who developed this approach to food science. The aims, meaning and misconceptions of MG are discussed in chapter 4 and the implications and importance for society are discussed in chapter 5. This is followed by description of relevant literature in the field, in chapter 0. The presented literature includes Paper I (*Scandinavian 'sushi': The raw story*), which connects traditional food science to developments in food culture and exemplifies how many of today's common fish preparation techniques have evolved as a result of the major need for preserving fish in the past. Moreover Paper II (*Molecular Gastronomy – a new emerging scientific discipline*) is presented which is a review of literature in the field. The sensory scientific elements of the review will be explained in most detail since part two of the thesis focuses more on chemistry and physics. Finally some concluding remarks on MG as a new scientific discipline are given in chapter 7.

3 SCIENTIFIC EXPLORATION OF GASTRONOMY, PAST AND PRESENT

In order to understand the origin of the term, Molecular Gastronomy, an insight into the historical background is given. Furthermore, examples of recent advances in the field are provided.

3.1 LOOKING BACK, THE 18TH AND 19TH CENTURIES

The search for a scientific understanding of cooking started several centuries ago. As early as in the 18th and 19th centuries, scientists explored food and cooking, and the scientific advances have had a large impact on the industrial production of food (This 2006b). Some early researchers and experimental chefs who have contributed to the scientific investigation of gastronomy are described in Table 1.

Table 1: Early contributors to the scientific investigation of gastronomy

Antoine Laurent de Lavoisier (1743-1794)

French chemist. Recognised the importance of utilizing scientific methods to understand food. Studied the process of stock preparation in 1783 by measuring density to evaluate quality (This 2006b). His work on stocks was evaluated in 2006 by This et al. (2006b).

Benjamin Thompson, Count Rumford (1753-1814).

Anglo-American physicist. His work included extensive investigations of the construction of fire places and kitchen utensils, first part published in 1799. Count Rumford was very eager to improve the work of chefs by improving their understanding and tools in the kitchen and he saw the potentials of using a scientific understanding to improve cooking. In his extensive description on construction of fire places he repeatedly calls for a better understanding of the science of cooking (Rumford 1969)¹.

Jean Anthelme Brillat Savarin (1755-1826)

French lawyer with a background and a great interest in chemistry and medicine (McGee 1990b). Brillat Savarin is the author of *The physiology of taste* from 1825, a classic book in gastronomy. The book takes a scientific and philosophical look at food and is concerned with good food and health issues. In the book Brillat Savarin argues that understanding science and physiology is needed to advance in gastronomy and emphasizes how much a greater insight in this field will benefit the society (Brillat Savarin 1999)².

Justus von Liebig (1803-1873)

German chemist. Did some work on meat and meat extracts. He started a production of commercial beef extract, which was to become the precursor of the bouillon cube (This 2006c).

Edouard de Pomiane (1875-1964)

French scientist and food writer. He explained the scientific principles of several traditional preparation techniques in order to demystify cooking (de Pomiane 2001). He argues that cooking can be rationalised and simplified, and considered a scientific technique (This 2007c).

The scientific field of food science developed in close collaboration with the food industry in the 19th and 20th century. The main applications of food science have traditionally been to provide safe and nutritious food for the masses in the most efficient and economical manner possible (Fuller 2001; Roudot 2004; Yek

¹ To avoid confusion, note that the year 1969 refers to publication of *The collected works of Count Rumford*

² The year 1999 refers to a modern English-language edition

and Struwe 2008), whereas the phenomena occurring during cooking have been neglected (This 2007c). Therefore the home or restaurant cook did not benefit from advances in food science while science and engineering supported the food industry greatly. Still today the professional chef rarely uses an understanding of chemistry and physics to explain, explore and improve his cooking (This 1999).

3.2 MOLECULAR GASTRONOMY DEVELOPS, THE 20TH CENTURY

A key person in exploring the gap between food science and cooking and defining a new sub-field of food science aiming at the restaurant and domestic kitchen was Nicholas Kurti (1908-1998). Nicholas Kurti was physicist at Oxford University specialising in low-temperature physics (Richards 1998; This 1999). He had a great interest in cooking and was very fond of Count Rumford (see Table 1). In 1969 the Royal Institution in London, founded by Count Rumford, celebrated its 170th anniversary. For that occasion Nicholas Kurti gave a lecture with the title ‘The physicist in the kitchen’, which was filmed by BBC. This was the beginning of many lectures, interviews, TV- and radio programs about the science of cooking by Nicholas Kurti. During this lecture he illustrated several scientific phenomena by small cooking experiments (Richards 1998; This 1999). On this occasion in 1969, Nicholas Kurti also raised the issue of scientists’ lack of attention to cooking and culinary innovation (Kurti 1969). In 1988 Nicholas Kurti and his wife published the book *The crackling is superb*, which contains short essays on food and drinks, by his fellow scientists (Kurti and Kurti 1988).

In the 1980’s Hervé This, a French chemist, investigated culinary proverbs in his lab in Paris. In 1986 Hervé This and Nicholas Kurti met for the first time and started to collaborate on their cooking experiments (This 1999). Hervé This achieved a PhD on ‘Molecular and Physical Gastronomy’ at the University of Paris in 1995, and continued his work in the field. Hervé This aims to assess the impact and relevance of the numerous prescription in cookbooks (This 2005).

Harold McGee, an American food writer with a degree in science and literature, also developed an interest in food science and cooking in the 1980’s. He studied the science and history of food and cooking and came to realize that food scientists had overlooked a lot of what goes on in the kitchen (McGee 2008b). The result of his effort to understand the science of cooking was in 1984 the first edition of *On Food and Cooking: The science and lore of the kitchen*, a compendium on food and cooking, reviewed by Nicholas Kurti (Kurti 1985). A few years later in 1990 he published *The curious cook: more kitchen science and lore* (McGee 1990a), which goes in depth with a number of traditional kitchen techniques. In 2004 the completely revised and extended second edition of *On Food and Cooking* (McGee 2004a) came out, which is a comprehensive encyclopaedia on food and cooking and a milestone in popular communication of scientific understanding of cooking.

In 1988 Elisabeth Cawdry Thomas, an anglo-american cooking teacher and friend of Nicholas Kurti, accompanied her husband (a physicist) at a meeting at the Ettore Majorana Center for Scientific Culture in Sicily, Italy. On this occasion Elisabeth Thomas and Professor Ugo Valdré of the University of Bologna met and agreed that the science of cooking was an interesting and undervalued subject. With the encouragement of Professor Ugo Valdré, Elisabeth Thomas proceeded with the idea of organizing a workshop on that topic at the same location. She asked Nicholas Kurti to be the organizer and in 1990 things began to take shape (McGee 2007; McGee 2008a; McGee 2008b; Thomas 2007).

In 1992 the first workshop was held, organized by Nicholas Kurti, Hervé This and Harold McGee. Although not officially an organizer, Elizabeth Thomas was the initiator of the workshop and a key person in the accomplishment and success of the workshop (McGee 2007; McGee 2008b; Thomas 2007). Until 1992 Nicholas Kurti had named the subject ‘Science and Gastronomy’, but on the request of the director of the Ettore Majorana center, Antonino Zichichi, to find a less ‘frivolous’ and more academic title of the workshop, the name was changed to ‘International Workshop on Molecular and Physical Gastronomy’ (McGee 2008b).

An additional five workshops were held at the same location; the last one in 2004. After the death of Nicholas Kurti in 1998, Hervé This changed the name of the workshop to ‘International Workshop on Molecular Gastronomy, N. Kurti’. The workshops included 30-40 participants of which most were scientist but about 20% were cooks. The focus of the workshops was on traditional kitchen preparations, for example stocks, how they work and how an understanding of the basic physics and chemistry involved might improve the preparation. The presentations and discussions have not been published (McGee 2008b).

Since then there has been a widespread transfer of food technology into the kitchens, not only tools and ingredients but also a rational and optimized working process. Several of the today’s leading restaurants in the world are examples of how a systematic approach to cooking together with a scientific insight in ingredients and techniques have lead to creation of highly innovative and outstanding dishes (Vega and Ubbink 2008). The Fat Duck (UK), elBulli (Spain) and Noma (DK), who were top three in 2010 in the acknowledged ranking ‘San Pellegrino World’s 50 Best Restaurants’ produced by a British magazine (Restaurant Magazine 2010) have research kitchens and staff dedicated to exploration of ingredients and new dishes.

3.3 RECENT ADVANCES IN THE FIELD, THE 21ST CENTURY

Of the large number of recent activities in science of cooking, those in France, Spain, New York City and Denmark are briefly described. A complete list of all MG related activities is not attempted but instead examples of important progress in research, teaching and science communication within the field of MG are given.

France

With Hervé This leading, the field has developed through articles, research activities, monthly seminars with chefs and scientists, courses and not least the creation of the foundation ‘Food Science and Culture’ in 2006 by the French Academy of Science (This 2006b; This 2007c). The educational effort has been considered important and in 2001 experimental workshops in flavour were created for French schools, which was followed by a new curriculum introduced at the culinary schools in France. Furthermore the European technology transfer programme (FP5), Inicon, has promoted collaboration between chefs, scientist, companies, and culinary schools between 2002-2005. In 2005 the Institute for Advanced Studies on Gastronomy was created with courses on Molecular Gastronomy.

Spain

Spain is well known in the world of gastronomy due to the very progressive and innovative chef Ferran Adrià and his restaurant elBulli, which has been in the front with using science and new technology to create new dishes. In 2004 Ferran Adrià together with the Catalan Regional Government started the Alicia Foundation which is a research centre focusing on health and gastronomy. In addition to the pure scientific research they conduct research in order to understand the history of food and gastronomic heritage (el Bulli 2010). They have a clear social mission by aiming at providing education and promoting better eating habits. Examples of projects are: hospital food, systematic study of products and kitchen appliances and introduction of young people to cooking to improve their eating habits (Alicia Foundation 2010).

New York

The Experimental Cuisine Collective in New York City, launched in 2007, is an association of food scientists, scholars, chefs, journalists and other people with an interest in food and cooking. They aim to provide a venue to gather and exchange knowledge on food. They want to enhance the scientific and social understanding of food and cooking by which they want to support innovative experiment-based culinary practice. Simultaneously they advocate for healthy and sustainable food production. Further they aim to introduce food and cooking to school children in order to create enthusiasm for physical science (Experimental Cuisine Collective 2010).

Denmark

At the Department of Food Science, University of Copenhagen, the new sub-field of food science was in 2004 announced to become part of the research activities. Thorvald Pedersen, a retired chemist and author of a book about the chemistry of cooking (Pedersen 2002), started up research and education activities at the Department of Food Science during the year of 2005 (Pedersen et al. 2006). In 2006 more activities were started supported by the Danish Research Council for Technology and Production Sciences including research and teaching. Gastronomy is now included in the curriculum of the BSc education in food science and a new MSc in 'Gastronomy and Health' has started.

4 DESCRIPTION AND MISCONCEPTIONS OF MOLECULAR GASTRONOMY

Traditional food science has generally neglected the phenomena occurring during cooking and the perception of the meal. Hence science has contributed surprisingly little to advances in cooking compared to how other arts have gained from scientific exploration (Kurti and This 1994; This 2006b; This 2009c). This forms the background for defining a new sub-field of food science. Molecular Gastronomy is characterised by a scientific approach to understanding and controlling physical and chemical processes occurring in food during preparation and consumption. Contrary to traditional food science, MG is primarily concerned with establishing the scientific basis for the quality and sensory experience of foods produced in small amounts that will be consumed relatively quickly and close to the place of production (van der Linden et al. 2008). As formulated by Blanck (2008): ‘Molecular gastronomists explore the physical changes that occur as food is prepared for human consumption and attempt to identify optimum methods of creating a dish for pleasurable flavour and texture’.

A brief definition, given by Vega et al. (2008): **‘Molecular Gastronomy is a scientifically oriented approach towards understanding the basic mechanisms occurring during cooking’.**

Since the term Molecular Gastronomy was first used, there has been a lot of misunderstanding and miscommunication by the public as well as by professional chefs and scientists, regarding the true/original meaning of it. The issue was raised at the ‘Second Symposium on Delivery of Functionality in Complex Food Systems’ held at the University of Massachusetts, Amherst (2007). The symposium discussion forms the basis of two publications: van der Linden et al. (2008) and Vega and Ubbink (2008). It has been further discussed and attempted clarified by Arboleya et al. (2008), Blanck (2008), This (2009c) and Yek and Struwe (2008). This issue will be explained in more detail below.

The use of science to explore and improve food preparations along with collaborations between scientist and chefs has led to new ways of cooking involving new kitchen technology and the use of new ingredients such as for example various additives formerly used in the food industry only. Throughout the last few decades professional chefs around the world have been experimenting with novel dishes resulting in some very experimental and challenging meals. These chefs have, with and without scientific insight, created a whole new cooking style, which is very much in contrast to traditional fine dining. This style of cooking is sometimes referred to as ‘experimental cooking’, ‘molecular cooking’, ‘science-based cooking’ (Arboleya et al. 2008; van der Linden et al. 2008; Vega and Ubbink 2008) or ‘new cookery’ (Adria et al. 2006). The new and experimental cooking trend, involving new technology and typical industrial ingredients like emulsifiers and stabilisers, has however also mistakenly been referred to as ‘Molecular Gastronomy’. Primarily due to the journalism and the related poor communication of the meaning of MG, the term is today widely associated by the public and by professionals with this new cooking style (van der Linden et al. 2008; Vega and Ubbink 2008).

Unfortunately several of the experimental and innovative restaurants have focused more on showing off new kitchen technologies than about serving the best possible food (van der Linden et al. 2008; Vega and Ubbink 2008). Vega and Ubbink (2008) refer to the so-called ‘elBulli effect’, implying the increasing number of restaurants that extensively use new technologies in the kitchen which is blamed for creating a culinary

atmosphere far from what traditional cooking was meant to be. This misconception has blurred the initial idea of improving and innovating the meal by use of science (Vega and Ubbink 2008). As a result MG has been and still is often associated mistakenly with a way of cooking and unfortunately moreover with a particular cooking trend that has received a great deal of criticism due to purely technological focus.

Consequently in 2006 some famous chefs³, known for their novel and scientific approach to cooking and use of new technology together with food writer Harold McGee wrote a 'Statement on new cookery' (Adria et al. 2006) in which they declare that Molecular Gastronomy doesn't describe their cooking or any cooking. They emphasize that they first of all strive to produce the best possible food and that a scientific understanding of food is a tool to produce excellent food. Hence they wish to cooperate with scientists and learn more. On the other hand they don't think technology should be used for the sake of novelty only but instead for obtaining the best possible food. This statement was followed by an article in the Observer (a UK newspaper) in 2007 with an interview of Heston Blumenthal on the same topic (The Observer 2007). In the discussions by van der Linden et al. (2008) and Arboleya et al. (2008) they debate whether a new term should substitute the historical but maybe less informative and today misunderstood term 'Molecular Gastronomy'. Most important, Arboleya et al. (2008) conclude that regardless of the name, collaboration between scientists and chefs should be encouraged.

Recent interviews with chefs from Michelin star restaurants in Europe (Cousins et al. 2010) confirm the large confusion about the MG term but despite the wide range of views on what MG is and what it attends to achieve, there was a general agreement by the chefs of the value of a greater scientific understanding and application of scientific techniques in order to improve culinary processes. The general view of the chefs was that a great chef needs a good depth of knowledge and experience to be a master technician. The chefs generally recognised that one must understand and apply the principles of science to achieve culinary mastery alongside with a will to enhance and to improve (Cousins et al. 2010). This survey demonstrates the interest and motivation by top chefs to explore the science of cooking in order to develop the art of cooking.

According to de Solier (2010), who investigated the MG concept and how it is practised by Ferran Adrià from elBulli and Hervé This, the difference in what Ferran Adrià is doing compared to the general aims of MG is that he brings science to high-end cooking whereas the original aims of MG cover a scientific insight in any meal, traditional as well as innovative (de Solier 2010). It is further explained how elBulli is much more than a restaurant. Six months of the year, the chefs spend their time in the research laboratory, creating dishes for the following year. Here they work together with scientists in a research team. Thus research, covering the chemical and physical processes of cooking, account for 50 percent of the culinary activity at elBulli (de Solier 2010).

Scientific communities have on several occasions honoured progressive chefs and recognized their expertise in the area on science and cooking. Ferran Adrià from elBulli in Spain was in 2007 awarded an honorary doctorate in chemistry by the University of Barcelona, Spain and a year later the University of Aberdeen, Scotland, decided to confer a similar degree on him (elBulli 2010). Ferran Adrià has in addition been collaborating with the school of Engineering and applied sciences at the very prestigious Harvard University since 2008 (Gudrais 2009). Heston Blumenthal from The Fat Duck in England was awarded an honorary

³ Ferran Adrià from elBulli (Spain); Heston Blumenthal from The Fat Duck (UK) and Thomas Keller from The French Laundry (France).

degree of Doctor of Science in 2006 by the University of Reading, England based on his dedicated research and exploration of culinary science (The Fat Duck 2010).

In conclusion, it is important to distinguish between the scientific discipline, Molecular Gastronomy, which investigates culinary transformation and the meal experience, and the new cooking style. The lack of differentiation between the scientific field on one hand and the application of new technology and ingredients in the kitchen on the other hand has caused a lot of debate in the media. These discussions have their roots in the general lack of knowledge on the origin of the term as well as what it encompasses. Despite the opposition to the term, scientific investigation of gastronomy is respected and requested by both chefs and scientists.

5 IMPLICATIONS AND IMPORTANCE FOR SOCIETY

Because food science has been mainly concerned with mass production there has been very little emphasis on taste and high quality foods and gastronomic food preparation. By recognizing the centrality of taste and by connecting science to gastronomy in order to understand culinary transformations and perception of a meal, general food quality can be improved (Roudot 2004). The passion and creativity of chefs can inspire food scientists and technologists to use food quality and perception as driving forces for their work instead of safety, ease of processing and costs (Vega and Ubbink 2008).

There is a need for high quality food in our society, to be eaten at home as well as when dining out. The food needs to be quick, delicious and convenient. The increasing demand by the consumer calls for more educated chefs and for cooperation between food industry, scientists and chefs. Due to the very different backgrounds, an interface between chefs and scientists is not straightforward. Thus chefs and scientists should be encouraged to pursue more scientific and culinary training respectively (Vega and Ubbink 2008).

Scientists need to understand the visions of chefs, even though they may be non-scientific and sometimes even irrational, in order to establish the important communication with chefs and moreover in order to translate the scientific concepts into practical guidelines. Ferran Adrià's collaboration with a range of scientists at elBulli is an example of successful interplay between chefs and scientists. Another examples is the collaboration between Heston Blumenthal (The Fat Duck) and among others physicist Peter Barham (Bristol University) and food scientist Andy Taylor (Nottingham University). Likewise the collaboration between Hervé This and chef Pierre Gagnaire in France is an example of fruitful teamwork (van der Linden et al. 2008).

MG provides a new focus for scientific research on food, exploring all aspects of quality and how to produce good meals. A better understanding of what precisely makes a food look and taste delicious may help in the mass production of high quality, safe and healthy foods (van der Linden et al. 2008). Research in MG and the related interaction between scientists and chefs can on one hand facilitate implementation of new ideas and recipes in restaurants and on the other hand challenge scientists to apply fundamental scientific understanding to the complexities of cooking. Scientists will expand their scientific understanding of many chemical and physical mechanisms beyond their usual working topics and in this way contribute to better foods in general. The benefits to the chef are to learn how to solve problems and explore new ideas using scientific methods. Introducing chefs to the way of thinking of scientists and teaching them a more scientific way of approaching a problem will provide a very useful tool for them to advance in their culinary practice (van der Linden et al. 2008).

This new focus for food research and the associated increased understanding and emphasis on science in the kitchen will not only provide interesting new challenges to scientists and new inspiration and tools for the chefs but it will also foster a general interest by the public in science. MG forms an ideal base to educate the general public about basic principles of science (Arbolea et al. 2008; van der Linden et al. 2008). An example of how scientific principles can be taught through kitchen experiments is the course on 'Science and Cooking: From Haute Cuisine to Soft Matter Science' provided by Harvard University (UK). The

curriculum covers phases of matter, thermodynamics and various chemical reactions and the course has inspired students to take further courses in science (Chang 2010; Harvard University 2010).

Using food and cooking as a way of introducing science to the public, not least children, will extend people's knowledge about food and health in general and improve cooking skills. This will give people a better background for making the right choices and controlling eating habits with great benefits for society. All together it will improve awareness of food and health and it will introduce essential knowledge needed for judging health and food quality issues (van der Linden et al. 2008). The relation between health and gastronomy has been overlooked for many years in the exploration for better nutrition and a better lifestyle. No matter what the nutritionists prescribe, the food must taste good and one must understand how to prepare well-tasting food. Furthermore well-tasting special foods are needed for certain groups like the elderly, children and the sick. Interactions between scientists and chefs will help meeting these demands (van der Linden et al. 2008). The Alicia foundation in Spain is an example of where such research and education is carried out. They focus on how collaboration between chefs and scientists can benefit society through research and education projects (Alicia Foundation 2010).

Recently scientific studies have shown that there is a need for more focus on cooking and high quality meals in our society in order to improve our health (Larson et al. 2006; Larson et al. 2009). The public has become sometimes fanatically health conscious so that pleasures of the table are rarely appreciated. This obsession is often misguided and the necessary insight into ordinary natural good food without any health labels is lacking. It may be the loss of good culinary instinct and the lack of emphasis by the food industry to produce mainstream high quality, healthy and convenient food that has led to the current situation (Pollan 2007). There are reasons to believe that focusing more on the enjoyment of a meal will be beneficial for our health. Studies in food sociology have shown large cultural differences in the way food functions in life. Americans generally associate food more with health and less with pleasure; they do the most effort to alter their diet but they don't consider themselves healthy eaters. Oppositely the French associate food more with pleasure and spend more time eating while eating less. This may influence health and partly explain the national differences in Cardiovascular disease, the so-called French paradox (Bow 2009; Rozin et al. 1999; Rozin et al. 2003). A new large research project at the University of Copenhagen, Denmark (OPUS), led by Arne Astrup, Professor in Nutrition, and Claus Meyer, affiliated Professor and gastronomic entrepreneur, focuses on the connection between gastronomy and health. The project aims to improve children's (and in the long term the general Nordic population's) health by creating and implementing a new tasty and appealing diet based on Nordic ingredients which at the same time is sustainable (Meyer et al. 2010; University of Copenhagen 2010).

Hopefully an increased understanding of food preparation and quality by the public combined with more culinary insight and understanding of quality by the food industry will lead to naturally satisfying and healthy meals in the future so that we can eat and enjoy food without consulting diet books.

6 LITERATURE IN THE FIELD

Examples of early literature in the field of science and cooking are given in section 3.1. More recent literature in the field of Molecular Gastronomy is introduced in this chapter with emphasis on the sensory scientific elements.

6.1 BOOKS

Examples of books (in English, German and Danish), explaining the science of cooking are given in Table 2. Example of literature published before the term Molecular Gastronomy became well known include the two volumes by Rietz and Wanderstock (1961): *A guide to the selection, combination and cooking of foods*. They contain a detailed description of the science of many preparation techniques and ingredients as well as appreciation of a meal. Rietz and Wanderstock (1961) recognize the gap between food scientist and chefs and aim to increase the understanding of food and flavour. Their work is comprehensive but to some extent also out of date and confusing. Several other books about the science of cooking have been published since then, in particular within the last 20 years.

Table 2: Examples of books explaining the science of cooking

Title (reference)
A guide to the selection, combination and cooking of foods (Rietz and Wanderstock 1961)
The science of food and cooking (Cameron 1973)
On food and cooking - the science and lore of the kitchen, 1 st edition (McGee 1984)
The epicurean laboratory - exploring the science of cooking (Seelig 1991)
Cookwise (Corriher 1997)
The inquisitive cook (Gardiner.A and Wilson 1998)
The science of cooking (Barham 2001)
Kemien bag gastronomien (Pedersen 2002) <i>The chemistry of gastronomy</i>
The new kitchen science (Hillman 2003)
Die Molekül Küche (Vilgis 2005) <i>The molecule kitchen</i>
Molecular Gastronomy (This 2006d)
Kitchen mysteries - revealing the science of food (This 2007b)
The curious cook (McGee 2008b)
Building a meal - from Molecular Gastronomy to culinary constructivism (This 2009b)

A recent initiative to communicate science on food and cooking is the publication of *The kitchen as a laboratory: reflections on science inspired by the kitchen*, a book edited by César Vega, Job Ubbink and Erik van der Linden, which contains peer reviewed articles on the science of cooking and pleasures of the meal. The book is expected to be published in 2011 and will contain Paper I (*Scandinavian 'sushi': The raw story*), which has been accepted for publication.

Paper 1 explains the science of some common fish preservation techniques and connects the development of these to development in Scandinavian food culture. In Scandinavia, there is a long tradition of eating raw

cured fish. The term ‘curing’ covers the use of antimicrobial techniques that preserve the product (prolong the shelf life). Drying is one of the earliest known means of preserving foods (Doe and Olley 1990). In warmer climates drying is still a common preservation techniques but, possibly due to the lack of sun in Scandinavia, other techniques such as salting and smoking have been developed and become a important part of our food culture. Preservation of fish by salting may be traced back to 3500 – 4000 BC, having reached its peak in the 18th and 19th centuries (Shenderyuk and Bykowski 1990).

The general principle of preservation is to make the conditions for microorganisms less ideal, which in many cases is done by lowering the availability of water. Salting lowers the availability of water by causing an osmotic pressure which result in removal of water from the fish. The salt also diffuses into the product (more details on the mechanisms behind diffusion are given in section 10.3.2, part two) and the dissolved salt lowers the water activity. Salt also causes the microorganism cells to dehydrate and thereby hinder their growth and reproduction (Horner 1992). Smoking, if carried out with heat, also causes removal of water but additionally the raised temperature by itself kills microorganisms. Smoking further preserves fish (or other foods) by the chemical components formed during smoking. Yet another possibility is to lower the pH of the fish (or other food) by lactic acid fermentation, or marinating in e.g. acidic acid (Bligh et al. 1988; Doe and Olley 1990; Horner 1992).

The physical and chemical transformations of the fish during these common preservation techniques extend the shelf life, but also change the flavour and texture of the food. Today we are less dependent on the preserving effect of these techniques and we salt, smoke and marinate our fish because we desire the resulting effects on the flavour and texture (Horner 1992). Through generations these preservation techniques have become common regardless of the need for preservation and the related changes in flavour and texture have shaped the Scandinavians’ preferences for fish.

Two very common fish preparations in Denmark today are salted pickled herring and the so-called ‘gravad lax’ (or ‘gravlax’ or ‘lox’) which both are served cold on bread often accompanied with a mild curry sauce and a sweet mustard sauce, respectively, as shown in Figure 1.



Figure 1: Two common Danish ways of serving raw preserved fish: salted, marinated herring with a mild curry sauce (left) and gravadlax with a sweet mustard sauce (right), both served on traditional Danish rye bread.

The term ‘gravad lax’ has its origin in the Scandinavian languages⁴, meaning ‘buried salmon’. In the middle ages people buried the salmon with salt and sugar in the ground, where it was left to cure. In addition to the preservation by salt, the buried salmon was preserved by action of salt-tolerant lactic acid bacteria. The bacteria caused a reduction in pH value by fermentation of sugar and the associated production of lactic acid. Today’s commonly eaten gravadlax is a lightly salted and unfermented product, produced by sprinkling salt, sugar and dill on the fish fillets and refrigerating for a couple of days. In order to enforce the contact between salt, sugar, dill and the fish and to press out excess fluid, the fish is weighed down during the cooling (McGee 2004b).

The very popular and traditional salted marinated herring is prepared by steeping the salted herring in water followed by marinating in sugar, spices and vinegar. The cold-served herring is sometimes referred to as ‘granddad sushi’, a name that demonstrates how this is the traditional way of eating un-heated fish in Scandinavia, in several ways similar to the Japanese sushi. The large influence of foreign food cultures in Scandinavia, such as Japanese, makes sushi today widely accepted although granddad might still prefer his salted marinated herring.

6.2 SCIENTIFIC PAPERS

Since MG is a developing sub-field of food science, scientific papers specifically aimed at gastronomic questions are still relatively few. This is related to the fact that there is no scientific journal for publishing such results. However a gastronomy journal, The International Journal of Gastronomy and Food Science by Elsevier and AZTI Technalia, is on its way (AZTI Tecnalia 2010). Hopefully this will be a useful literature platform for exchange of scientific knowledge in the field of gastronomy in the future.

Although few scientific papers aim specifically at increasing our understanding of culinary techniques and preparation of gastronomic meals, a large number of papers have contributed to our current understanding of food, cooking and perception of the meal. Paper II (*Molecular Gastronomy: a new emerging scientific discipline*) reviews the broad field of research which has increased our basic understanding of food properties and preparation techniques, thus relevant for our understanding of what makes an enjoyable meal. The literature reviewed contains not only cooking related aspects but also how production techniques may affect the flavour of food and how the complex perception of food determines the final meal experience. The literature in the review can accordingly be divided into three main categories, as also illustrated in Figure 2, that are all important to the quality of the meal:

1. **Production:** how does production of vegetable and animal food ingredients affect flavour and texture?
2. **Preparation:** how do the culinary unit operations (chopping, cooking etc) affect the flavour and texture?
3. **Perception** of the meal: what effects the final perception of the meal when it is served and consumed?

⁴ In Danish: ‘gravet laks’.

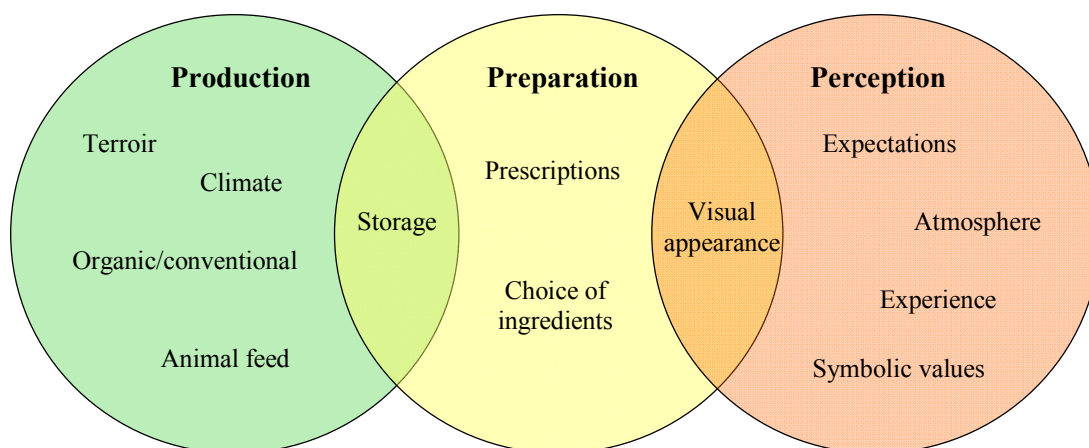


Figure 2: The three scientific categories in the field of Molecular Gastronomy as presented in Paper IV, a review of literature in the field. In each of the three categories examples of relevant research topics are given.

An example of a research topic in the first category, **production**, is the effect on flavour of organic versus conventional production methods. It is commonly believed that organic produced food tastes better, but there is little scientific evidence to support this. A review by Bourn and Prescott (2002) shows that the studies conducted on this topic are inconclusive and contradictory. Bourn and Prescott (2002) further question the scientific methods used in several of the studies reviewed. Generally the effect of conventional versus organic production may easily be confounded with other factors. Consequently thorough investigation of this topic is needed to draw any conclusions.

Another topic in the **production** category is the effect of feed on the flavour of meat. A number of scientific studies have shown a clear effect of feed on composition of the meat and meat flavour (Melton 1990; Poste 1990). For example it has been shown that the fatty acid composition of the feed is reflected in the meat and that this affects the flavour of the meat (Scheeder et al. 2001). Fatty acid composition may further indirectly affect the meat flavour since a higher degree of unsaturation increases the chances of lipid oxidation resulting in off flavours (Melton 1990; Poste 1990).

An example of literature in the second category, **preparation**, is the study by McGee (1984) on whisking egg whites in a copper bowl. It is shown that it takes longer to beat egg whites to a given consistency in a copper bowl than in a glass bowl, but copper improves the foam stability. Other examples are Paper III and Paper IV on stock reduction which will be presented in part two of the thesis.

The introduction of a symbolic language describing the physical structure of food by Hervé This can also be regarded as belonging to this category. The new formalism is known as the Complex Disperse Systems formalism, CDS (This 2003; This 2005). Hervé This argues that this can be used to classify food preparations, as for example sauces, and to invent new dishes. The strength and weaknesses of the CDS are discussed by Vega and Ubbink (2008) who conclude that despite the potential of CDS to visualize the building blocks of a dish, there is room for improvement and they point out some shortcomings of the system. In addition to the CDS formalism, Hervé This later introduced the Non Periodical Organizational Space formalism, NPOS, which describes the arrangements of objects in space. He suggests that by combining the two formalisms, a good description of the microstructure and organization of food and drugs can be obtained (This 2007a).

The third category, **perception**, contains a large range of topics within the field of sensory science, psychology and neurophysiology. Perception of a meal is determined by much more than just the flavour and texture of the food since all our senses play a role in perceiving the meal and thus experiencing a meal can be regarded a multisensory experience (Spence 2008). Understanding what affects one's perception of a meal is extremely complicated but such insight is of great importance in serving a good meal in a restaurant as well as in the production of food by the industry (Meiselman 2008). The food industry is already well aware of many issues in this category, such as how the sound of the packaging may influence the perceived flavour of the product or how the colour of a product is crucial to the consumer's acceptance of food. In restaurants such insight can be used to produce superior meal experiences (Spence 2008). Heston Blumenthal from The Fat Duck actively uses his understanding of perception of food, implying the complex interaction of all senses, in designing dishes at his restaurant (Blumenthal 2008a; Spence 2008).

More examples of research in the **perception** category include studies of interaction between colour and odour determination. Several studies have found a strong influence of visual information on the perception of odours. One example is the study by Morrot (2001), which shows how 54 wine tasters described the odour of a white wine dyed red as a red wine in terms of odour. Thus the tasters clearly made use of the visual information and to some extent discounted the olfactory information in their determination of odour. Another study by Zampini (2008) showed how identification of flavours in fruit flavoured drinks was eased if the drink was coloured appropriately.

Other studies have assessed the role of sound in the perception of food. One example is the study by Zampini (2004) showing how the perceived crispiness and freshness of potato chips could be affected by modifying the sound produced during the biting action. Crispiness and freshness were perceived more intense when the overall sound level increased. The review by Zampini and Spence (2010) presents the growing research in this field and assess how auditory stimuli can affect people's food choices. Spence (2008) refers to his work with Heston Blumenthal at The Fat Duck on adding sound to a dish and how that affects the perceived intensity of a flavour and the pleasantness of the dish.

Generally scientists seek a deeper understanding of how information is generated in the brain, for example how one flavour can affect another, or how sound and colour can influence the perceived flavour of a meal. Such studies require measuring of brain activity and the study of how the brain collects and puts together information (McGlone 2008; Prescott 2008; Schifferstein and Spence 2008; Spence 2008; Ward 2008). The review by Meiselman (2008) concludes that product experience is the interaction of a person and a product in a particular context or situation, which means the same food is experienced differently depending on the environment.

Perception of a meal is further controlled by our genetic inheritance and previous experiences. The context in which we have been introduced to a food is very important to whether we like or dislike the particular food, and hence preferences are culturally dependent. Repeated exposure to a food increases the pleasantness of the food (except if the food causes illness). Preferences are thus also due to change depending on what we eat, hence we can 'learn' to appreciate food. Our expectation of a meal is build upon our previous experiences and this can greatly affect preference of a food, (Prescott 2008). Mielby and Frøst (2010) showed in a restaurant setting how 'liking' depended on familiarity with the served dishes of the diners.

They further showed that the verbal presentation of a dish affected the acceptance by the diner of the least liked dishes.

Both the colours of a meal and visual appearance as well as our memories concerning the food all set up an expectation of the meal before eating it. The extent to which our expectations are met or exceeded is a key in the pleasure of eating. Our response to food is part of a cognitive process in which our brain integrates information both from the sensory qualities as well as from our past experiences with that food (Prescott 2008). The brain receives information on taste, odour, texture, temperature, colour and sound of the food which all combine to give the overall flavour of the food. This information is processed in the brain in relation to our expectations to the food which is build on our previous experiences. A large mismatch between expected experience of a food and the perceived experience can result in a dramatic effect on the pleasure (Yeomans and Chambers 2008).

Yeomans et al. (2008) studied what happens when cues prior to ingestion suggest a flavour which is very different to the actual flavour characteristics. In this study they served smoked-salmon ice cream (a classic dish from The Fat Duck) to the participants and investigated the effect of changing the expectations by changing the label on the ice cream. The experience of the food when eaten was strongly disliked when labelled as *ice-cream*, but accepted when labelled as *frozen savoury mousse* and thus in accordance with the actual flavour. Labelling the food as ice-cream moreover resulted in higher ratings of saltiness and savouriness. Thus this study demonstrates that a large contrast between expected and actual sensory qualities can result in a strong negative response and furthermore an increase in the perceived intensity of the unexpected sensory qualities, as in this case, the saltiness and savouriness.

The study by Klosse et al. (2004) examined the palatability of a restaurant meal. By interviewing chefs he studied the criteria for a good meal and defined six culinary success factors (CSF). These are: 1) name and presentation fit the expectation; 2) appetizing smell that fits the food; 3) good balance of flavour components in relation to the food; 4) presence of umami; 5) a mix of hard and soft textures; and 6) high flavour richness. The first two are related to an agreement between expected and experienced flavour, as has been explained above. The third, fourth and sixth CSF are concerned with the flavour, balance and intensity. The fifth CSF is concerned with textures and suggests a variety of textures in a dish while the sixth CSF suggest a general high flavour intensity. The suggested CSF's were tested in an restaurant study with where diners were served variations on the same meal with either all CSF's present or leaving out some. Results obtained from the 26 diners in the study showed that the meal variation with all CFS's present was preferred. Consequently the six CSF's were suggested as a tool to improve and develop dishes.

Yet another topic in the **perception** category is the combination of food and drink - how to match food and drink? This has been investigated in several studies, of which one deals with the combination of Hollandaise sauce and wine (Nygren et al. 2001) and the others deal with the classical combination of cheese and wine (Harrington 2005; Harrington and Hammond 2006; Madrigal-Galan and Heymann 2006; Nygren et al. 2002; Nygren et al. 2003a; Nygren et al. 2003b). The approach in several of these studies is to study the effect of consuming a drink or food item (e.g. a cheese) prior to intake of another food or drink (e.g. wine). The effect on the perceived flavour of the food or drink is analysed and related to the preceding consumption of food or drink. By using this approach, Madrigal-Galan and Heymann (2006) showed how prior intake of cheeses affects the perceived flavour of red wines. They found that some attributes in the wines, such as astringency,

bell pepper, and oak flavour, significantly decreased when the wine was evaluated after tasting cheese. Only butter aroma in the red wine was significantly enhanced by prior intake of cheese.

The phenomenon of interaction between foods has been studied more generally since most food is eaten as meals and flavour interactions between individual components of a meal may occur. Aaslyng and Frøst (2008) investigated the effect of basic tastes on the perception of pork patties using a similar approach as described above. They showed how bitter and sour taste influenced the flavour of the patties by increasing their own basic taste in the patties but reducing other flavours (sour, piggy, metallic/liver). Further they showed that salt reduced the bitter taste and increased the sour taste, whereas sweet accompaniment had no influence on the flavour of the pork. This was further investigated by Aaslyng and Frøst (2010) in another study on flavour of pork patties in which they confirmed that interactions occurred, but further showed that in more complex meal combinations, the effects are smaller.

7 CONCLUDING REMARKS

Molecular Gastronomy is an emerging sub-field of food science which investigates everything that relates to preparation and enjoyment of a good meal. In contrast to traditional food science it focuses on small scale preparation and the quality of the meal in all its aspects. Molecular Gastronomy bridges the gap between science and gastronomy and has large potential to contribute to better meals and better health in the future. A greater understanding of meal preparation and meal perception can potentially increase the value of meals eaten in canteens and other public places as well as at home. Thus it has implications for the entire catering industry as well as for the home cook.

The lack of scientific understanding by the chef and the purely industrial aims of scientific research in food science have caused the existing gap between science and cooking. MG aims to fill out the gap between science and cooking and in this way obtain high quality food at home as well as when eating out. MG thus promotes interaction between chefs and scientists which has great potential. It is however important to recognize the challenges of such collaboration. Chefs and scientists have very different backgrounds, different 'languages', different goals and they work with different time scales. Hence successful collaboration requires determined and open-minded researchers as well as chefs who have the will and the practical opportunity to spend the time needed to build up this collaboration and define common goals. Due to the usual work conditions for both chefs and researchers with a tight schedule and a constant pressure to present results, this is difficult. More recognition of work in the field of MG and more culinary training of food scientists could possibly improve their opportunities to work in this field. Likewise would chefs, regardless of their interest in the classic or the innovative kitchen, benefit from more scientific insight in cooking. A greater impact on the basic scientific mechanisms related to cooking in the education of chefs could give chefs an increased chance of producing classical dishes to perfection. It could moreover boost their creativity since a basic understanding of how things work opens up many new possibilities. Learning to question things and seeking the answer through a basic scientific understanding is a way for the chef to avoid failures and to invent novel dishes.

Another challenge when working in the field of MG is that the term is often misunderstood. To a large part of the public and scientists the background and the meaning of MG is not clear. MG is mistakenly often associated with the increasing number of restaurants who are using high technology and creating highly innovative dishes, although these are not always driven by science. On the other hand many restaurants have initiated a new style of cooking that incorporates an understanding of science and technology, resulting in a range of new challenging dishes which makes a visit to the restaurant a new multi-sensory experience. This style of cooking which was labelled 'New cookery' by Adrià et al. (2006) is often characterized by being experimental and highly scientific, independent of the term used to describe it.

In conclusion, it is important to communicate that MG is not a style of cooking but it is an emerging sub-field of food science. MG focuses on the transformation of food during cooking and the sensory phenomena associated with eating. This branch of science is applied at some innovative restaurants.

8 MEAT STOCKS, AN INTRODUCTION

Part two of the thesis is concerned with the preparation of meat stocks, in particular the so-called reduction of the stock which means boiling the stock down. It starts with the definition and uses of stocks in section 8.1, along with the history of stocks and sauces in section 8.2. The brief history section comprises the development of stock based sauces as we know them today and their significance in our cuisine as well as some early scientific advances in meat flavour extraction. Chapter 9 gives details on the preparation of stocks which include a presentation of common cookbook prescriptions. Following this, chapter 10 examines relevant scientific literature in the field of flavour science which encompasses perception and analysis of flavour, meat flavour formation and various aspects of physical chemistry explaining volatility of aroma compounds. The theoretical examination is followed in chapter 11 by a closer investigation of meat stock reductions based on the work published in Paper III (*Flavour development during beef stock reduction*). Chapter 12 describes an investigation of meat stock reductions with red wine, the topic of Paper IV (*Beef stock reduction with red wine, effects of preparation method and wine characteristics*). Chapter 6 rounds off part two of the thesis by a discussion on the scientific base for preparation of meat stocks and suggestions for continuing studies on meat stock.

The literature studied for the scientific exploration of meat stocks comprises peer-reviewed papers and reviews as well as textbooks, when referring to elementary scientific understanding. In addition, popular scientific literature on the science of cooking, primarily by Hervé This and Harold McGee, are used in the identification and discussions of the problems. Moreover a number of cookbooks were consulted, providing the background for identification of the problems and generation of hypotheses. Generally, prescriptions and explanations in cookbooks are taken as the starting point and further identification of problems and discussions are based mainly on scientific peer-reviewed literature but also some popular scientific literature.

8.1 DEFINITIONS AND USES OF MEAT STOCKS

A definition by The Culinary Institute of America (2006): ‘A stock is a liquid prepared by simmering meaty bones from meat or poultry, seafood and/or vegetables in water with aromatics until their flavour, aroma, colour, body, and nutritive value are extracted. The liquid is then used to prepare sauces, soups, and as a braising and simmering cooking medium for vegetables and grains’. A similar description is given by Beck et al. (1978), author of *Mastering the art of French cooking*. Traditional stock recipes are divided into brown and white, where the brown stocks are characterised by a preliminary roasting of the ingredients which gives a more so-called ‘rich’ flavour to the stock (Larousse 1993; Peterson 2008; The Culinary Institute of America 2006).

Meat stock is the base for many traditional French sauces (Larousse 1993). Auguste Escoffier, who will be introduced in section 8.2, states in his famous cookbook *Le Guide Culinaire* that ‘sauces are one of the most important components of cookery’ and ‘it is therefore impossible to devote too much care and attention to their preparation’ and ‘it is to the production of perfect stocks that the sauce cook should devote himself’ (Escoffier 1979)⁵.

⁵ Originally published in 1903, the year 1979 refers to a modern English-language edition

After preparing the stock, the volume can be reduced by boiling off water. The aim of reducing a sauce is to improve its flavour and consistency. Reduction is also used to obtain concentrated essences of for example white wine or vinegar or of red wine with onions, which is a preliminary process for many sauces (Montagne 2001). The reduction of the stock is carried out to some degree, or not at all, depending on the use of the stock. Many sauces call for at least some degree of reduction of the stock (Larousse 1993).

If the stock is boiled down to around 10% it is referred to as meat glace. Due to the intense flavour of meat glace it is used in small quantities to lend flavour to sauces and other stock based dishes (Escoffier 1979). A demi-glace refers to a less extensive reduction, to about 25-40 % of its original volume which often is thickened with starch to make up for the smaller concentration of gelatine (more about gelatine in section 10.2.4, part two). Tomato puré or paste is often added to make up for the less intense flavour and colour. The demi-glace has the advantages of requiring less time for reduction and giving a larger final volume. Demi-glaces are the base of many classic French sauces which are given their individual characteristic by adding various other ingredients like herbs, vegetables and wine and finally enrichment and thickening with butter and cream (Peterson 2008). Related terms are described in Table 3.

Table 3: Description of stock related terms

Jus	The traditional <i>jus</i> describe the natural liquid from drippings of roast. The flavour of a <i>jus</i> can be reinforced with additional meat trimmings and vegetables (Peterson 2008).
Coulis	<i>Coulis</i> refers to a stock to which fresh meat is added in several turns leading to a stock high in gelatine and flavour. The traditional <i>coulis</i> , popular in the 17 th and 18 th century, was made by three successive poaching of meat and the result was extremely flavourful compared to a reduced stock. The method of intensifying the flavour by using an already prepared stock to poach meat for a new batch, is also referred to as double stock, and if the process is repeated a triple stock. (Peterson 2008).
Essence	<i>Essence</i> refers to the extract of meat or vegetables which was used as an ingredient in many sauce recipes before the 20 th century. <i>Essences</i> are made in the same way as stock but using much less liquid than usual to ensure a very concentrated flavour of the main ingredients (meat, fish, mushroom etc), that can be used as an ingredient in sauces (Escoffier 1979).
Glaces	<i>Glaces</i> are stocks that have slowly been cooked down (reduced) to a syrupy consistence. <i>Glaces</i> can be used as a sauce after finishing with butter or cream, or they can be used to strengthen a sauce or another stock based preparation for which the stock used was too weak (Escoffier 1979; Larousse 1993; Peterson 2008; The Culinary Institute of America 2006). The meat glace is thickened by reduction (due to increasing gelatine concentration) only, which requires a reduction to approximately 10% of original volume. The classic <i>demi-glace</i> , which became standard base for brown sauces in the beginning of the 20 th century, is a less reduced stock which is thickened further with starch (Peterson 2008).
Broth	Similar to stocks, a clear and flavourful liquid with some viscosity. The distinction between the terms is that a <i>broth</i> can be served as it is whereas stocks are used as an ingredient in the production of other dishes. A <i>consommé</i> is a perfectly clear <i>broth</i> served as a soup (The Culinary Institute of America 2006).
Soup	Stock based soups may only differ from sauces by being less concentrated in flavour (McGee 2004c).

As will be described further in the following history section, the preparation of large batches of stock and the use of these as a sauce base became a substitute to the earlier so-called ‘integral sauces’ which were prepared directly from the juices released from the fish or meat. The difficulties in preparing integral sauces are partly that fish and meat rarely supply enough flavour to make sufficient sauce and partly that it is impractical in a

restaurant setting to prepare the integral sauce for each dish. Due to these problems chefs developed stocks as a convenient and less expensive way of preparing sauces (Peterson 2008).

8.2 HISTORY OF STOCKS AND SAUCES

Sauces are flavoured liquids that accompany other ingredients like meat, fish vegetable or grain with the purpose of enhancing their flavour. A wide variety of sauces, hot and cold, exist across different parts of the world. In France sauce making has been developed into a systematic art which has become the heart of their national cuisine and further has set the international standards for fine dining (Herbst and Herbst 2009). Details on the changes in culinary traditions in Europe, started in France, from medieval times to the 18th century, are described by Pinkard (2009).

Sauces played an essential role in the dining of the ancient Roman elite (McGee 2004c). Roman sauces were made with honey, *garum* (a liquid mixture made with fish entrails) and a variety of spices and herbs. Wine and vinegar were also often used in Roman cooking but the wines were often flavoured with spices and honey. Sauces were also sometimes flavoured with wine that had been boiled down (Peterson 2008).

Roman and Medieval sauces generally contained sweet and sour ingredients as well as spices. Often they were made with vinegar or cider as the only liquid component (Hyman and Hyman 1999). In the middle ages, meat juice is first known to have been used for sauce making. Some medieval sauce recipes prescribe 'binding' the cooking liquid of meats and fish with bread, almond, and egg yolk (Peterson 2008). In the 14th century, chefs had discovered thickening by boiling off water, the so-called 'reduction' (McGee 2004c).

The sauces of our own time have their roots in the period between the 14th and 17th centuries, when the very spicy and sour flavours typical of the Middle ages were increasingly rejected by the social elite. Instead there was an increasing use of butter and cream together with meat juices (Hyman and Hyman 1999). Meat juices became the central element of fine cooking, and a very large range of soups and sauces based on extraction of meat juices were developed (McGee 2004c). In the 17th century the preparation of intensively flavoured sauces, based on meat juice from roasted meat (*jus*), were popular. Huge amounts of meat were used in order to get enough meat juice to make the sauce. In the 17th and 18th century the *coulis* became the common base for brown sauces. *Coulis* was prepared by subsequent poaching of meat batches in the resulting stock by which the stock gradually became thicker and more intense in flavour. The method of preparing sauces individually for each dish was very expensive and inconvenient (Peterson 2008).

In the 18th century a greater systematization of the basic sauce components was brought about by Antonin Carême (1784-1833), a renowned French chef. He contributed greatly to the culinary progress after the French revolution and in particular began to organize the almost infinite number of sauces and thereby helped the chefs to structure their work. The sauces were divided into four sauce families, each headed by a basic sauce which conveniently could be prepared in advance so the chef didn't have to prepare each sauce from scratch any more. Antonin Carême's four basic sauces are espagnole, velouté, allemande and béchamel (Larousse 1993; Peterson 2008; Sokolov 2007). The three first of the four sauce families introduced by Antonin Carême were based on meat stock and hence this marked the beginning of the stock as a basic kitchen preparation. In this way the very expensive sauce preparation based on pure reduced meat juice was substituted with the stock prepared from bones, meat and meat scrapings, as we know it today (McGee

2004c; Peterson 2008). In this time period the French cuisine had a profound influence on the other European countries and became the cuisine of choice for high-status dining in Europe and also outside Europe (Day 2009).

Since the 18th century chemists too had an interest in meat stock preparation. The French chemist, Antoine-Laurent de Lavoisier (1743-1794), founder of modern chemistry, studied meat stock preparation by using density to evaluate its quality, which has recently been further investigated by This et al. (2006). Further scientific investigations on meat and advances in analytical chemistry took place, which were the preliminary steps toward the current knowledge on meat and extraction of meat flavour. Based on the knowledge at the time, Brillat Savarin (introduced in Table 1) explains meat composition and the flavour extracted from meat in his book *The physiology of taste* from 1825 (Brillat Savarin 1999). Brillat Savarin refers to the ‘osmazone’ which he believed was the single substance responsible for the special qualities of meats and any foods made with meats. In his book he gives many details on meat and its components, the effects of cooking it and advice on cooking. Brillat Savarin was very focused on understanding the science of cooking and using this to support chefs in their preparation techniques. Further studies on meat and in particular extraction of meat flavour into liquid were done by the German chemist Justus von Liebig (1803-1873), who started a production on commercial beef extract, which was to become the precursor of the bouillon cube (This 2006c).

In the beginning of the 20th century Auguste Escoffier (1846 - 1935) further simplified and re-structured the French sauces in his book *Le Guide Culinaire* published in 1903. The 4th edition was translated into English in 1979 (Escoffier 1979). During this time sauces became the heart of classic French cooking and gradually became the standard for fine cooking in the Western world. The demi-glace (reduced stock thickened further with starch) became the standard base for brown sauces and is still today a basic kitchen preparation (Larousse 1993; Peterson 2008; Sokolov 2007).

In the late 20th century many chefs began to break out of the rigid standards for fine dining (defining the 1970’s ‘nouvelle cuisine’). Until then, wealthy diners expected first of all consistency in a dish, whereas today the sophisticated diner appreciate the use of local food and originality (Peterson 2008). Many of the complex dishes of earlier periods were replaced by simpler and more subtle modes of preparation. Terroir⁶ became central in defining the new cuisine and restaurant customers began to seek an authentic local cuisine experience (Miele and Murdoch 2002).

The culinary revolution brought new sauces and dishes from other food cultures into the world of fine dining, but the classic white and brown sauces are, although less often used today, still a keystone in our cuisine. In the 21st century restaurants and home cooks that rely on the basic stocks and stock reductions for their soups and sauces often take advantage of premade stocks produced by the food industry, and hereby save time for other elements of fine cooking (The Culinary Institute of America 2006). Hence the demand for industrially produced high quality stocks has increased, not least because stocks are used for much more than traditional French sauces. A greater knowledge of the science behind a superior stock can support not just the chef, but also the food industry in producing high quality stocks for the restaurant, the growing catering business and the home cook.

⁶ Originally denotes the special characteristics that is related to the geography of a particular wine grape variety

9 PREPARATION OF MEAT STOCK

The aim of a meat stock preparation is to turn water into a full flavoured liquid with an increased viscosity and a clear appearance. This is obtained in two steps, first cooking of ingredients in water by which flavour is formed and extracted and the viscosity increases (due to gelatine extraction as will be described later) and second boiling down (reducing) the strained stock by which the flavour intensity and viscosity of the stock increase. Further steps and various precautions are taken to ensure a clear appearance of the stock. In this chapter the preparation techniques and examples of the large number of prescriptions are presented along with some suggested explanations by the cookbook authors. The prescriptions on stocks and stock reductions, as presented below, are all concerned with how to obtain the best possible flavour, texture and appearance of the stock.

9.1 THE BASIC STEPS IN MEAT STOCK PREPARATION

The basic steps in preparation of brown meat stock are roasting meat, bones and vegetables, then cooking the roasted ingredients with herbs and spices in water possibly followed by boiling the stock down (Peterson 2008). This process is illustrated in Figure 3. The basic ingredients can be divided into three categories: 1) meat and bones 2) vegetables (mirepoix), herbs and spices (bouquet garni) and 3) liquid, which usually is water or a too thin stock but for example tomato juice or lemon juice may also be added (Larousse 1997).

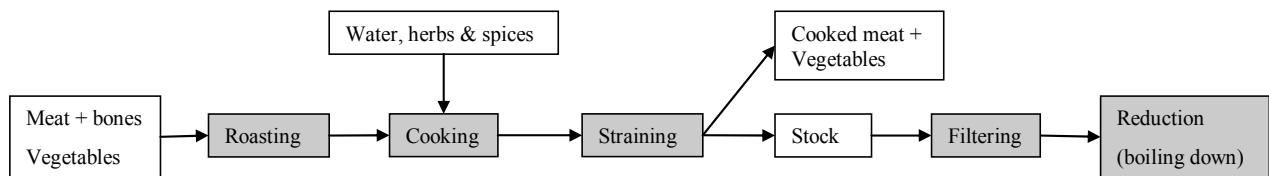


Figure 3: Main step in common preparation of reduced brown meat stock.

9.2 COOKBOOK PRESCRIPTIONS AND EXPLANATIONS

In cookbooks a large number of prescriptions specify how to prepare the stock in more details. In the following sections some common prescriptions and advice from cookbooks are presented together with suggested explanations by the cookbook authors (whether correct or not). It is not attempted to explain or explore the large number of prescriptions scientifically but it serves to illustrate the large number of scientifically relevant questions related to meat stock preparation. The presented prescriptions will further introduce some of the problems concerning stock reduction which will be explored scientifically in chapter 11.

9.2.1 Cooking

Often recipes give more detailed instructions on the order of adding the ingredients to the stock pot. Escoffier (1979) advises to add the meat after having cooked the additional ingredients for 12 h whereas others recommend to add vegetables and herbs later in the cooking process in order to obtain the optimal

flavour (Larousse 1993; Larousse 1997; The Culinary Institute of America 2006). Other common prescriptions on the cooking of stocks are listed in Table 4 which includes conflicting advice.

Table 4: Prescriptions on meat stock preparation

Prescription (reference)
<p>Start with cold water and heat slowly (Brillat Savarin 1999; Corriher 1997; Escoffier 1979; Larousse 1993; Larousse 1997; Peterson 2008; Sokolov 2007; The Culinary Institute of America 2006)</p>
<p>Never boil only simmer (Brillat Savarin 1999; Corriher 1997; Escoffier 1979; Larousse 1997; Peterson 2008; Sokolov 2007; The Culinary Institute of America 2006)</p>
<p>Add only hot water to a simmering stock (Larousse 1993; Larousse 1997)</p>
<p>Add only cold water to a simmering stock (Peterson 2008; Roux 1996)</p>
<p>Skim frequently throughout the cooking time (Escoffier 1979; Larousse 1993; Larousse 1997; Peterson 2008; The Culinary Institute of America 2006)</p>
<p>Cook in an open pot (This 2007e)</p>
<p>Use a pot that is taller than wide in order to minimize evaporation (Corriher 1997; The Culinary Institute of America 2006)</p>
<p>Roasting meat and bones with tomato paste aids the clarification process (Larousse 1993)</p>
<p>Prescribed cooking time on brown beef stock:</p> <ul style="list-style-type: none"> ○ 12-15 h before addition of meat (Escoffier 1979) ○ 10-12 h (Larousse 1993) ○ 6-8 h (The Culinary Institute of America 2006) ○ 5-6 h or more if bones are cooked by themselves before adding meat (Peterson 2008) ○ Minimum 4 h (Larousse 1997) ○ 2½ h, 'long cooking can be detrimental since the stock becomes heavy and loses its savour' (Roux 1996)

Among the several prescription, 'starting with cold water' and 'only simmer' are on of the more common, and have been recommended since the 19th century (This 2009a). These prescriptions are generally coupled to achieving a clear stock with optimal flavour.

Larousse (1993; 1997) recommends to start the cooking process with cold water to allow for maximum extraction: 'Beginning with hot water prematurely coagulates the albumin in the bones, inhibiting its interaction with the water and the subsequent extraction of gelatine, flavour and nutrients' (Larousse 1997).

This explanation may originate from the 19th century, or before; at least a similar explanation for this prescription is given by Antonin Carême and Brillat Savarin (Brillat Savarin 1999; This 2006c).

Larousse (1993; 1997) further explains that simmering is essential to the natural clarification process: ‘As the stock simmers, heat convection causes the liquid to move rhythmically around in the pot while the albumin slowly coagulates trapping impurities as the stock moves through it’ and further he explains ‘the vigorous activity of a boiling liquid prohibits the slow careful collection of impurities, resulting in a cloudy stock, while slow gentle simmering promotes clarification and a gentle release of flavour from the ingredients’ (Larousse 1997). Larousse (1993; 1997) moreover recommends to regularly skim the stock throughout the cooking process in order to remove the fat, albumin and impurities collected at the top.

Peterson (2008) recommends to start with cold water because ‘if hot water is added to meat, it causes the meat to release soluble proteins (albumin) quickly into the surrounding liquid, that immediately coagulate into fine particles that cloud the stock. When cold liquid is used and slowly heated, the proteins contained in the meat (or fish) coagulate in larger clumps that float to the top where they can be skimmed (Peterson 2008). Peterson (2008) further explains, in line with Larousse (1993; 1997), how simmering allows the release of fats and proteins into the stock which appear as a scum on the top, whereas ‘if boiling they are churned back into the stock and become emulsified, the result is a cloudy stock with a dull, muddy greasy flavour, which only worsens during reduction’ (Peterson 2008).

The advice on starting with cold water is also explained in *Cookwise* (Corriher 1997), a cookbook with suggested scientific explanations. According to Corriher (1997) if using hot water the starch from the vegetables will gel and minimize flavour extraction. Corriher (1997) also likewise explains how boiling must be avoided until all fat has been removed, because otherwise the fat will be emulsified and form a cloudy fatty stock.

The idea of keeping the temperature under the boiling point upon cooking of meat is something that was already discussed by Count Rumford (introduced in Table 1): ‘It is evident that the process of cookery which is called boiling, may be performed in water which is not boiling-hot’ and further ‘I well know from my experience, how difficult it is to persuade cooks of this truth; but it is so important that no pains should be spared in endeavouring to remove their prejudices and enlighten their understanding’ (Rumford 1969).

9.2.2 Reduction

Having prepared the stock it can then be reduced by ‘boiling it down’, yet often cookbooks recommend to keep the stock pot on low heat so it only simmers, as also recommended for the cooking step (Larousse 1993; Peterson 2008; The Culinary Institute of America 2006). Others report reduction over high heat at full boil (Roux 1996; Sokolov 2007). The effect of simmer versus boil will be discussed in chapter 11.

Prescriptions on the length of reduction are often not specified in cookbooks, but instead cookbooks commonly prescribe the extent of reduction based on the decrease in volume (which will be expressed as the concentration factor in later chapters). For example a 10% reduction is prescribed in order to obtain a glace. Sometimes such prescriptions are followed by an estimated time (Larousse 1993; Peterson 2008; Sokolov 2007; The Culinary Institute of America 2006). Peterson (2008) recommends not to ‘overreduce’ because it

will make the stock lose too much aroma due to evaporation and will make them too sticky due to the high gelatine content (Peterson 2008). The effect of reduction time and decrease in volumen will also be discussed in chapter 11.

Other prescriptions on the reductions step are associated with obtaining a clear reduced stock, as also discussed in relation to the cooking step. Larousse (1993) states that a clear stock reduction can be achieved in two ways 1) by slow and careful simmering of the stock, which enables a natural clarification process and 2) by clarifying the stock through a separate procedure. During reduction it is recommended to skim the simmering stock regularly to remove scum and fat, as also prescribed during the cooking step. It is further recommended to strain the stock and transfer it into a smaller pot from time to time during the reduction (Escoffier 1979; Larousse 1997; Peterson 2008; The Culinary Institute of America 2006). In the comprehensive cookbook by The Culinary Institute of America (2006), it is further suggested to skim the stock with the purpose of making the stock less exposed to spoilage and hence extending the shelf life.

9.2.3 Obtaining a clear stock

Many prescriptions are associated with getting the stock as clear as possible and these are often coupled with an explanation in cookbooks. The general explanation is that some proteins and fat can make the stock cloudy but also that precautions can be taken to avoid this; these include starting with cold water, heating slowly and avoiding boiling. McGee (2004b) confirms the importance of the recommended cold start as well as the slow heating and simmering throughout the cooking and reduction. He explains that by following these prescriptions, it allows the soluble proteins to escape the solids and coagulate, slowly forming large aggregates that either rise to the surface where they can easily be skimmed off or settle onto the sides and bottom of the pot. A hot start on the other hand produces many tiny protein particles that cloud the stock and a boil will churn the particles and fat droplets into a cloudy suspension and emulsion. This explanation is in line with those by Peterson (2008) and Larousse (1993; 1997), except for the fact that the cookbook authors refer to 'albumin' only. According to This (2009a), when these explanations were first suggested in the 19th century, albumin was a general term used to refer to the entire class of proteins. Clarification by means of proteins is also the idea behind the traditional stock clarification method which involves addition of egg whites to the stock. This (2007e) explains how the added egg whites coagulate around the cloudy particles; and the resulting scum can be removed from the top of the stock pot.

McGee (2004b) additionally explains that leaving the pot uncovered will lead to surface cooling that further dehydrate the surface scum which then becomes easier to skim. Further McGee (2004b) explains that the preliminary roasting of meat and bones for brown stock has the advantage to coagulate the surface proteins so that they don't cloud the stock (McGee 2004c).

10 FLAVOUR SCIENCE – AN EXAMINATION OF RELEVANT LITERATURE

The above arguments, statements and prescriptions regarding meat stock preparation motivate an examination of the scientific background related to the process of turning water into a meat-flavoured liquid. Fundamental knowledge in the field of flavour science, including perception and analysis of flavour, meat flavour formation and important aspects of physical chemistry which relate to volatility of aroma compounds are described in this chapter. Further, more speculative suggestions of what may happen upon cooking of meat in water are presented. The presented scientific knowledge and theories are important for the interpretation of results and for discussions on the experimental studies of beef stock reduction, presented in section 11.2 and 12.3.

10.1 PERCEPTION AND ANALYSIS OF FLAVOUR

Food contains a large range of molecules that act as flavour when entering our sensory system. Humans perceive these molecules through the mouth and the nose. The molecules that we perceive through receptors in the mouth are the non-volatile taste compounds, whereas the molecules that are perceived through the nose (directly or retronasal) are the volatile aroma compounds, sensed as smell. In addition to taste and smell, the trigeminal flavour sense is responsible for the sensations of eg. pungency, astringency and temperature, often referred to as mouthfeel. The term ‘flavour’ often refers to the combined sensation of taste, aroma and the trigeminal responses (Lawless and Heymann 1999). Other senses, as vision and hearing, also play an important role in the experience of food as discussed in section 6.2 (part one).

10.1.1 Perceiving the flavour molecules

The flavour molecules must reach our sensory receptors in order to be perceived. The non-volatile taste compounds must be transferred to the saliva upon eating in order to reach the gustatory system. On our tongue we have receptors for sweet, sour, salt, bitter and umami, which means that these sensations can be induced from molecules acting on the tongue. These are commonly referred to as the five basic tastes. The mechanisms behind taste perception are reviewed by Chandrashekar et al. (2006). In addition to these current well documented basic tastes, studies on mice and humans have suggested the existence of a fat receptor in the mouth, which may explain our taste for fat (Gaillard et al. 2008; Mattes 1996). Further studies in this field may reveal several other taste receptors.

The sensation of aroma is only achieved when volatile molecules are released from food and transported to the nose. This happens even before the food is consumed but upon consuming food the aroma compounds are transferred retronasally to the olfactory system in the nose. It is thus the partitioning of volatile aroma compounds (described in more details in section 10.3.1) between the food phases and into the air phase upon eating that determines the characteristic volatile profile, sensed as aroma (Overbosch et al. 1991; Preininger 2006; Reineccius 2006; Taylor 1998; Taylor 2002). Several studies have investigated the release of aroma in the mouth. The various flavour release models that have been proposed generally assume that volatile compounds in the oil phase of the food must first be transferred to water (saliva) in order to reach the olfactory system (de Roos 1997; de Roos 2000; de Roos and Wolswinkel 1994; McNulty and Karel 1973; Taylor 1996; Taylor 2002).

As will be explained in more detail in section 10.3.1, non-volatile compounds in the stock, such as proteins and oil, may limit the aroma compounds from evaporation during cooking of a stock. These may, however, on the other hand also limit the release of the same compounds upon eating it, which affects the perception (Overbosch et al. 1991; Preininger 2006; Reineccius 2006; Taylor 1998; Taylor 2002). Because the same mechanisms apply to flavour retention upon cooking and release upon eating, a low volatility in the food product may result in a high retention during heating (usually positive) but also in a poor release during eating (usually negative) (de Roos 2006; de Roos and Mansencal 2003). It is important to remember that not all volatile compounds are aroma compounds, and that the perception of the aroma compounds depends not only on the concentration in the food and the release of the compounds upon eating but also on the individual concentration threshold for perception (Schifferstein and Spence 2008; Wysocki and Wise 2004).

The trigeminal receptors are located in the mouth and are accounted for the sensation of e.g. the perceived fizz from carbon dioxide, the burn from chilli, the pungency from mustard and the astringency from red wine or unripe fruit. These sensations are commonly described as the *mouthfeel* of a food. The astringent sensation, also described as a dryness of the mouth, is an important sensation in red wine and is associated with the presence of polyphenolic compounds (tannins⁷). It has been shown that binding between salivary proteins and phenolic compounds causes the astringent sensation but organic acids in wine can also induce astringency (Jackson 2002).

10.1.2 Analysis of flavour

In scientific studies of food, the analysis of flavour is of great importance since flavour is obviously a major sensory property of food. There are two main approaches to analysis of flavour, either analysis of the flavour molecules or analysis of the human perception of the flavour of a food. These approaches are often combined. The first approach requires some analytical tools appropriate for the questions to be investigated and an understanding of how the concentration of molecules may affect the perceived flavour. Analysis of perceived flavour, sensory analysis, on the other hand, requires standardized ways of using humans as 'measuring devices'. Both approaches to analysis of flavour contain a large number of methods and procedures that all have their advantages and disadvantages. In the study of beef stock flavour in Paper III and IV the flavour has been analyzed using a combined approach, a descriptive sensory analysis along with gas chromatography, and in paper IV also high-performance-liquid-chromatography.

The studies on beef stock focus on the volatile aroma components. Gas chromatography (GC) was used to study their quality and relative quantity of these. The volatile compounds are first extracted from the food, usually by means of collecting the so-called head space, the air above the food which contains a fraction of the volatile compounds. The headspace extraction techniques are divided into the static and the dynamic (purge-and-trap) methods but in addition a more recent method, solid-phase microextraction (SPME), is available (Ettre 2001). After extraction, the sample is injected in gas form to the chromatographic column and carried through the column by a carrier gas (helium or nitrogen). The compounds are separated on their way through the column due to the varied affinity of the compounds to the column material (stationary phase). The volatile compounds elute separately (at least to some degree) from the column with a characteristic retention time. A detector is attached to detect the quantity of the eluting compounds, and this

⁷ Condensed flavonoids, often referred to as tannins, are made up of usually epicatechin and catechin. The resultant larger polyphenols (500-5000 molecular weight) are precipitable with protein and are perceived astringent (Singleton, 1988).

data is presented in a chromatogram. The principle of the commonly used Mass-Spectrometer (MS) detector is to ionize the compounds which result in charged particles that are separated according to their mass-to-charge ratio. The detected ion signal is processed into a mass spectra which is characteristic of the compound detected. Based on data-base information the mass-spectra can be used to (tentatively) identify the compounds and thus MS provides quantitative as well as qualitative information (Skoog et al. 2007).

While GC only measures the volatile aroma compounds, the non-volatile taste compounds can be measured by other methods. One method to study non-volatile compounds is high performance liquid chromatography (HPLC), which has been used in Paper IV to study the concentration of some sugars, organic acids and phenolic compounds. HPLC is another chromatographic technique that separates the compounds on a column and a detector provides the characteristic retention time of the eluting compounds (Skoog et al. 2007).

Knowing the concentration of flavour molecules in a food still only gives limited information on how the food is perceived since there is no simple stimulus-response relationship, but rather a complex reaction to stimuli leading to an individual perception of flavour depending on personal history and the frame of reference (as also discussed in section 6.2, part one). A sensory study gives direct information on how a food is perceived. It is unfortunately not straightforward to get a good description of the flavour of a food since humans are different and describing flavour is difficult. In order to overcome these obstacles several sensory methods have been developed to give the most precise description of the flavour of a food. Depending on the aim of the study the method must be chosen. Generally the methods lie within three categories: discrimination (do the products differ), descriptive (how do the products differ) and affective (how well are the products liked) (Lawless and Heymann 1999). In the case of the beef stock studies (Paper III and IV) the aim was to observe the changes in flavour depending on the preparation conditions, and in this case a descriptive analysis was chosen. Descriptive sensory analyses are characterised by using a so-called 'trained panel' and by asking the panellists to rate or rank the chosen descriptors (words describing the taste, aroma or mouthfeel of the food). A trained panel has the same vocabulary and has been trained to describe the food in a uniform way. By using several repetitions a meaningful interpretation of the described flavour can be made, and significant differences can be found. The subsequent statistical treatment of the data is crucial to a sensible interpretation of the results. A two-way analysis of variance (ANOVA) is the a common statistical analysis on this type of data and this will elucidate which food samples are differentiated and in which descriptor (Lawless and Heymann 1999). Multivariate analysis such as Principal Component Analysis (PCA) gives a more visual interpretation of the results. Multivariate correlation, e.g. Partial Least Square (PLS) regression, can be performed to find possible relations between sensory and analytical data. The use of such multivariate tools for analysis of sensory data are discussed by Heymann and Noble (1989).

10.2 MEAT FLAVOUR

Although all ingredients, including vegetable and herbs, play a role to the meat stock flavour, meat is the main ingredient and thus only formation of meat flavour is described. The taste of raw muscle is bland, being only slight sweet, sour, salt or bitter, but the desirable taste and odour of meat develops upon cooking as a result of thermally induced reactions and complex interactions with precursors derived from lean and fatty tissue of the meat. A large range of volatile aroma compounds are produced and these, as well as several

non-volatile taste compounds present in the meat, give the complex sensation of meat flavour (Mottram 1991).

During preparation of meat stocks, which involves heating of meat and other ingredients in water followed by reduction, the water is turned into a meat-flavoured stock. In order to understand this transformation, the literature on meat flavour has been examined. A large number of scientific studies have investigated meat flavour formation and have attempted to identify which volatile and non-volatile molecules that are important for what people recognizes as meat flavour (Farmer and Patterson 1991; Gasser and Grosch 1988; Hornstein and Wasserman 1987; Melton.S-H. 1999; Mottram 1998).

10.2.1 The role of the non-volatile compounds

Generally, the most important non-volatile taste compounds in meat are amino acids, peptides, organic acids, sugars, salts as well as the so-called umami compounds which act as flavour enhancers and increase the savouriness of meat. Compounds such as creatine, carnosine, triglyceride lipids and some amino acids further contribute to the mouthfeel of meat (Imafidon and Spanier 1994; Mottram 1991).

Macleod (1994) has reviewed the taste-active compounds in flavour of beef and provides an overview of the sources of sweet, salt, sour, bitter and umami taste, the five basic tastes. Sweetness is associated with various sugars as well as some amino acids and peptides. Sourness is related to both organic and inorganic acids; saltiness to the presence of inorganic salt and bitterness stems from amino acids and peptides (MacLeod 1994). The umami taste sensation is provided by glutamate⁸, the anion of glutamic acid (an amino acid), and the 5'-ribonucleotides, guanosine monophosphate (GMP) and inosine monophosphate (IMP) as well as some peptides (Bellisle 1999).

Umami, originally a Japanese term meaning delicious, is best described as savoury, meaty or brothy. Since the 1980's umami has been accepted as a basic taste and receptors in the mouth have been identified. Umami is by itself not palatable but it enhances flavour intensity of other foods. Thus the umami compounds are commonly referred to as flavour enhancers and used as additives in the food industry. A large synergistic effect exists between glutamate and the ribonucleotides, meaning the threshold of glutamate is markedly lowered by the presence of IMP and GMP. Of the ribonucleotides, IMP is found primarily in meats and GMP is more abundant in plants. The chemical structures of glutamate, IMP and GMP are shown in Figure 4.

In addition to these commonly known umami compounds, research in the field have identified some peptides with an umami taste. Examples are Noguchi et al. (1975) who reported identification of some umami tasting peptides from fish protein hydrolysates and Yamasaki and Maekawa (1978) who identified an octapeptide with a pleasant meat flavour from hydrolysed beef. Through further research in the field, more umami compounds may be discovered.

⁸ This is often referred to as the sodium salt, monosodium glutamate, MSG, which is commercially available as a flavour enhancer

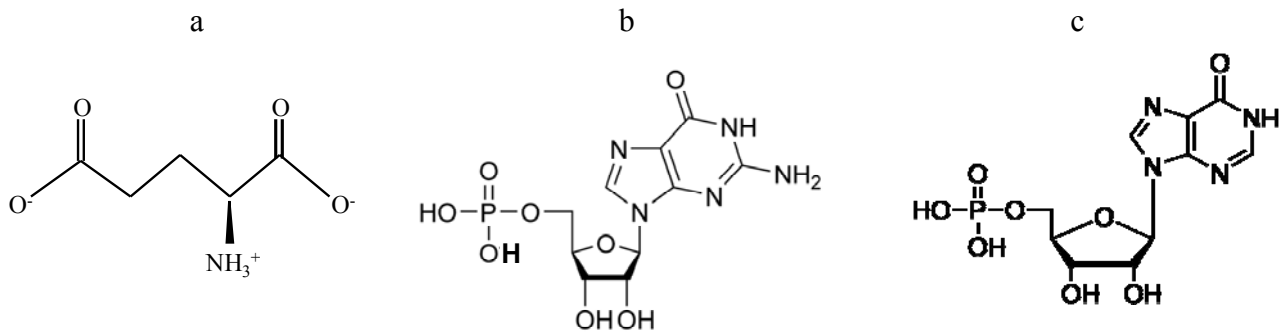


Figure 4: Chemical structure of umami compounds: a) Glutamate, the anion of glutamic acid, b) guanosine monophosphate (GMP) and c) inosine monophosphate (IMP). GMP and IMP are both 5'-ribonucleotides.

The similarities between umami and what Brillat-Savarin in 1825 described as the essence of meat taste and named the ‘osmazone’ are noticeable. Brillat-Savarin was not able to identify the key component of the ‘osmazone’ but still he considered the discovery of the osmazone ‘the greatest service by chemistry to food science’ (Brillat Savarin 1999).

Another important group of taste compounds are the amino acids and peptides, which arise from hydrolysis of proteins, as occurring upon cooking of meat in water (Liekse and Konrad 1994). Amino acids and peptides elicit all five basic tastes (sweet, sour, bitter, salt and umami). In general, the more hydrophobic amino acids (as for example L-Leucine and L-phenylalanine) taste bitter, whereas the more hydrophilic (as L-Serine and L-asparagine) taste neutral or sweet. Peptides consisting of the bitter tasting amino acids are also bitter (Nishimura and Kato 1988). The bitter peptides have received substantial attention since they are responsible for the unpleasant bitter flavour in some processed foods in which protein hydrolysis has occurred. This is reviewed by Maehashi and Huang (2009). The amino acid, glutamic acid, as already explained, elicit umami taste when present as the carboxylic anion, and as also explained some peptides have moreover been reported to have a meaty flavour and an flavour enhancing effect resembling that of umami compounds.

Besides contributing to taste by themselves, non-volatile compounds act as precursors to the formation of volatile aroma compounds. The major precursors of meat flavour can be divided into two categories, water-soluble compounds and lipids. The main water-soluble flavour precursors are suggested to be sugars, free amino acids, peptides, nucleotides, and other nitrogenous components, such as thiamine (Imafidon and Spanier 1994; Mottram 1991). Meat flavour formation depends on the production of the meat since the formation of precursors in the muscle may be influenced by the animal’s diet and stress conditions (Hornstein and Wasserman 1987).

10.2.2 Volatile compounds and meat aroma

In addition to the great importance of the non-volatile compounds to meat flavour, the volatile compounds which account for the meat aroma, are very important to the overall flavour characteristic associated with meat. These are formed during the cooking of meat (Imafidon and Spanier 1994; Mottram 1991).

The number of volatile aroma compounds identified in meat, in particular beef, is large, as illustrated by Mottram (1991) who lists a large number of volatile compounds of different chemical classes. The large

number of volatiles is partly explained by the various preparation methods used in the different studies (Mottram 1991). Only some of the volatiles present in cooked meat are important to the meat aroma. According to Hornstein et al. (1987) the most important categories of volatiles for meat aroma are: carbonyls, furans, pyrazines and sulphur-containing compounds as shown in Figure 5.

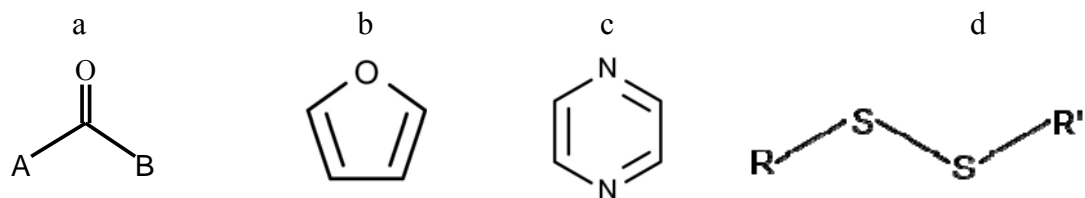


Figure 5: Chemical structure of some common volatile aroma compounds in meat: a) basis structure of carbonyls which include e.g. aldehydes, ketones, esters and carboxylic acids, b) a furan, the term also covers other compounds which contain this aromatic ring, c) a pyrazine and d) an example of a sulphur-containing compound, a disulphide.

Aroma development upon cooking is highly dependent on the heat treatment, thus roasted meat tastes rather different than boiled meat. Boiled meat is characterised by the predominance of sulphur compounds as for example thiols, sulfides and disulfides. Roast meat aromas are associated with heterocyclic compounds such as pyrazines (Mottram 1998). Further is it reported that the higher the degree of heating, the greater the concentration of Strecker aldehydes and lipid oxidation products (MacLeod and Ames 1986).

10.2.3 Important chemical reactions

The major chemical reactions leading to meat aroma upon cooking (heating) have been identified to be Maillard reaction and lipid oxidation, though oxidation produces off-flavours as well (Imafidon and Spanier 1994; Mottram 1998). Both are important classes of flavour reactions, accounting for flavour generation in many foods. They will be briefly described here:

Lipid oxidation is a chain reaction that is initiated by oxygen or by free radicals on unsaturated lipids. The primary products are hydroperoxides, which are further cleaved to form aroma compounds (Frankel 2005). Oxidation of unsaturated fatty acids of meat lipids provides a wide range of aroma compounds that are important to meat aroma. These are aliphatic compounds such as hydrocarbons, alcohols, aldehydes, ketones and carboxylic acids as well as lactones, furans and alicyclic hydrocarbons (Melton.S-H. 1999; Mottram 1991). Lipid oxidation products seem to be important in determining the aroma differences between species. Thus it is generally believed that the difference in flavour between meat species is mostly related to the fat composition of the meat. Whereas the lean meat provide precursors for the meaty flavour, the fat provides the precursors for the species-specific flavours (Mottram 1998).

Maillard reactions take place at raised temperatures and are largely responsible for the characteristic flavours of cooked meats which are developed from the proteins and sugars present. The Maillard reactions are a complex series of reactions starting with a reducing carbonyl compound and an amine. The reactions produce both volatile aroma compounds and coloured pigments, thus contributing with aroma and colour to the meat. Maillard reactions often occur in parallel with Strecker reactions and caramelization and lead to many important aroma compounds which can be divided into three groups: 1) simple sugar dehydration and fragmentation products such as furans, 2) amino acids degradation products such as Strecker aldehydes, 3)

products from further interaction such as pyrazines (Nursten 2005; Nursten 1981). Details on the Maillard reactions are given by Nursten (2005) and Bayenes et al. (2005).

In addition to lipid oxidation and Maillard/Strecker reactions, degradation of thiamine has also been shown to produce important aroma compounds (sulphur compounds) in meat (MacLeod 1994). The chemical structure of thiamine (Vitamin B₁) is shown in Figure 6. More details on the proposed mechanism of the thermal degradation of thiamine is given by Guentert (1990).

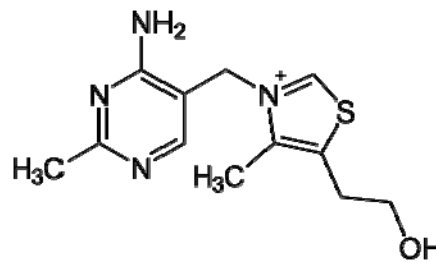


Figure 6: Chemical structure of thiamine (Vitamin B₁)

10.2.4 Formation of flavour and texture in meat stock

Heating meat in water, as when cooking a stock, is a way of preparing meat characterised by the fact that temperature does not exceed 100°C. This process causes denaturation and hydrolyses of the meat proteins which leads to the formation of flavour active molecules in the meat as well as in the surrounding liquid, as described in more detail in the previous sections. Addition of other non-meat ingredients to the stock provides additional flavour to the stock.

Simultaneously with flavour development in the stock during cooking, the texture changes. Extraction of gelatine from collagen (connective tissue) into the surrounding water is the obvious explanation for the observed increase in viscosity in the meat stock. Meat, and especially bones and skin, are rich in collagen (Walstra 2003a). The non-volatile protein, gelatine, is most likely concentrated during reduction of the stock, which explains the increase in viscosity upon reduction of the stock.

As mentioned above, gelatine is derived from collagen, the connective tissue of muscle. Collagen is the principal structural protein of connective tissue. The different types of collagen are composed by three polypeptide strands that form a triple helix (the tropocollagen molecule) which are assembled into fibres (Tornberg 2005). The fibres are cross-linked and the linkages increase in number and strength as the animal grows. Thus hard-working old muscles have more cross-linked connective tissue, which provide a toughness to the meat upon cooking (Aberle et al. 2001).

Upon heating the solubility of the collagen increases, which leads to partial unfolding (the triple helix unwind) of the protein. This process starts at around 60°C and is characterised by contraction of the collagen molecules. Further heating causes hydrolysis and the collagen fibres to dissolve and form gelatine. Higher levels of heat-stable cross-links, as in older animals, provides more resistance to the break-down of collagen upon heating (Tornberg 2005). Mahendrakar et al. (1989) showed how the heating solubility of collagen from lamb decreased with age. They further showed that cooking under pressure (using an ordinary kitchen pressure cooker, 1 kg/cm²) resulted in greater solubility.

Gelatine is readily soluble in water at temperatures above 40°C. It forms a viscous solution of coiled polypeptide chains, which upon cooling (around 20°C) form partly stacked helices, that results in forming of a thermo-reversible gel. The minimum concentration for gel formation is 1% (Walstra 2003b). Due to the thickening or gel-forming properties of gelatine, it is used as a thickener in many industrial food products and it becomes the natural thickener of stocks and sauces.

A relative high concentration of gelatine is needed to thicken a warm sauce with gelatine because of the poor thickening properties at elevated temperature. Very high gelatine concentration gives a undesired sticky consistency to the stock and the sauce will form a gel as it cools down on the plate. Therefore a sauce may be augmented with starch or fat which can further thicken the sauce (McGee 2004c). This (2007d) has performed some experiments to investigate the role of gelatine in thickening stock. The results suggest that the gel-forming property of gelatine alone is not sufficient to give the desired thickening effect to a hot sauce. Instead he suggests that also surface-activity of gelatine plays a role by supporting the emulsion formed when whisking fat (butter or cream) into the meat stock upon sauce preparation.

Several questions arise from this basic understanding of turning water into stock e.g. how do various preparation factors like time and temperature affect the qualities of the stock, what is the role of oil in the process, which molecules are most important to the formation of a meat stock or simply how does one obtain the best possible stock? The cookbooks tell us what to do but the prescriptions are very diverse and do not account for the difference in the ingredients being used. Nor do the cookbooks give us any understanding of the effect of the different cooking factors. The cooking conditions, e.g. time and temperature, can be expected to have an important effect on the extraction and formation of the molecules which give flavour and texture to the meat stock. The optimum cooking conditions may well be dependent on the ingredients e.g. type and amount of meat, bones and other ingredients. Moreover the optimal choice of cooking conditions will depend on the desired outcome of the stock, which is related to the use of the stock. It may therefore not be possible to define the optimal conditions but it is essential to understand the effect of the various factors that can be controlled and optimized upon preparation of a meat stock. A number of studies have investigated the first step in meat stock preparation, the actual cooking of the stock, in which the flavour is formed and extracted from the meat. These studies are reviewed and discussed below. The second step, the reduction of the meat stock, will be dealt with in chapter 11.

The cooking time (extraction time) for a meat stock is often prescribed in recipes, and as shown in Table 4, the prescriptions for cooking time are very diverse. The cooking time is likely to be of great importance to achievement of flavour and texture in the stock. As also discussed by Ubbink (2010), the cooking process must allow sufficient time for extraction and formation of flavour as well as extraction and hydrolysis of collagen. On the other hand the longer it is cooked, the more aroma may be lost due to evaporation. This is apparently recognized by Roux (1996), who warns against cooking too long in his cookbook on sauces. Ubbink (2010) suggests that the extraction of the gelatine is the slowest step as opposed to formation of meat flavour. Hence he suggest not to cook any longer than it takes to obtain enough hydrolysed collagen (gelatine). He further suggests to cook the bones by themselves before adding the additional ingredients as also suggested by Peterson (2008) in his recipe on brown stock for meat glace. The recipe on stock by (Escoffier 1979) likewise recommends to extract the flavour from meat after having cooked the additional ingredients for 12 hours. The optimum cooking time with regard to collagen hydrolysis is dependent on the

size of the bones and meat pieces, and on the age of animals due to the variability in cross-linking of the collagen.

A few scientific studies have investigated the effect of cooking time, temperature etc. on the extraction of flavour from meat into the water. These studies generally aimed to understand how to obtain the best/strongest beef stock (broth) flavour by cooking meat in a sodium chloride solution and also aim to identify the important non-volatile flavour compounds. Seuss et al. (1990) found that the best flavour in a simple stock made from beef heated in a 0.75 % sodium chloride solution was obtained at 85°C as opposed to 55, 65, 75 or 95°C. A cooking temperature of 85°C generated the highest concentration of IMP and glutamate as well as a high concentration of other free amino acids. Cambero et al. (1992) did a similar study and also found the strongest brothy flavour at 85°C as opposed to 55, 65, 75 or 95°C. The result illustrated the importance of IMP, GMP and peptides to the beef stock flavour. Another study by Cambero et al. (2000b) investigated the effect of cooking time, temperature, meat cut size (cubes/minced/paste), meat-water ratio and the sodium chloride concentration on the perceived flavour by means of discrimination and descriptive sensory analyses. They found that the most intense beef flavour was obtained by using minced meat, a 0.75 % sodium chloride solution, a meat-water ration of 1:1 or 1:2 and by cooking at 85°C for 1h. Cooking temperatures below and above 85°C were also found to give a reasonably good meat flavour intensity if cooking time was adjusted accordingly (longer at lower temperatures and vice versa). A further study by Cambero et al. (2000a) studied in more detail the relation between flavour compounds and the cooking temperatures. The results confirmed the relation between beef flavour intensity and the nucleotides, IMP and GMP. They further correlated flavour intensity to other compounds which may have an effect on flavour (D-ribose, creatinine and small nitrogen compounds) but this relation was not studied further. The study found that off-flavour developed at temperature higher than 95°C. One more study in the same category was performed by Pereira-Lima et al. (2000). They found a positive correlation between beef flavour and some amino acids (glutamic acid, asparagine, lysine and methionine) and peptides (anserine, carnosine). An inverse relationship to beef broth flavour was found with other amino acids which is interpreted as a sign of Maillard reactions.

Together these studies on beef stock provide some information on extraction conditions and their effect on meat flavour formation when cooking beef in water with a low concentration of sodium chloride. The results suggest that the optimal extraction (cooking) temperature is below the boiling point; the most intense flavour is obtained at around 85°C. The results indicate that the optimum extraction time when cooking at 85°C under the specified conditions was 1 h but also that the flavour obtained depends on both time and temperature, so these two factors must be adjusted correspondingly. Although extraction may be longer when using larger pieces of meat, the results suggest that extraction of meat flavour is a lot faster than the cooking times commonly prescribed for stock preparation (see Table 4). As also suggested by Ubbink (2010) the often recommended long cooking times can be explained by the slower collagen hydrolyses which are likely to be the most time consuming process during cooking of a stock with meat and bones. The studies further correlate some known taste compounds (nucleotides, amino acids and peptides) to meat flavour intensity and generally confirm the importance of umami compounds for beef stock flavour. The studies do not provide any understanding of the effect of cooking conditions on formation of volatile compounds. Nor do the studies include hydrolysis of collagen and the resulting extraction of gelatine from the bones. Thus no conclusion regarding the optimal cooking conditions for a beef stock can be drawn based on these results.

10.3 PHYSICAL CHEMISTRY OF FLAVOUR

Various aspects of physical chemistry can help us to understand the behaviour of the volatile aroma compounds in the stock during cooking. Since aroma compounds by definition are volatile, a loss must be expected upon heating of a stock in an open pot, as when reducing the stock. The extent to which the various kinds of aroma compounds are lost due to evaporation in a simmering stock pot is, however, not straightforward to predict and has not previously been studied. In order to make some reasonable hypotheses regarding the aroma loss from a simmering or boiling stock pot, the relevant literature on retention of aroma from a food will be examined.

Flavour retention is a general issue in food processing which is relevant to address in this context since many desired aroma compounds are likely to be lost upon cooking and reduction of a stock. Nevertheless not all volatile compounds are aroma compounds contributing to the desired flavour. The loss of some of the volatile compounds upon cooking may have no effect on the flavour or even a desired effect if the compound gives an off-flavour.

10.3.1 Distribution of volatile compounds at equilibrium

A simmering stock consist of three phases: water, oil and gas (bubbles of water vapour leaving the stock) in which the volatile compounds can be present. Depending on their relative affinity for the three phases, the volatile compounds distribute between the water, gas and oil phase of the food (Preininger 2006; Taylor 1998). Thus the affinity, which depends on the chemical structure, determines the volatility of the compound. Volatile compounds that reach the gas phase (air above the stock or vapour bubbles leaving the stock) are lost from the stock. Therefore the distribution between phases is important to understand in order to predict the effective volatility and the behaviour of volatiles upon cooking, and not least release and perception of the same molecules in the mouth. Additionally the binding of aroma compounds to protein may further affect the effective volatility of aroma compounds in a meat stock.

Figure 7 illustrates the equilibrium distribution of volatile compounds between phases as well as binding of proteins in a stock model. The partitioning is generally described by partition coefficients (K), which is a value that represents the distribution of a volatile compound between phases in a system at equilibrium (Preininger 2006; Taylor 2002). The distribution between water/gas and oil/water and the related coefficients will be further described below. The descriptions below generally assume that the conditions concerning an ideal mixture are met, meaning the activity coefficients are equal to one.

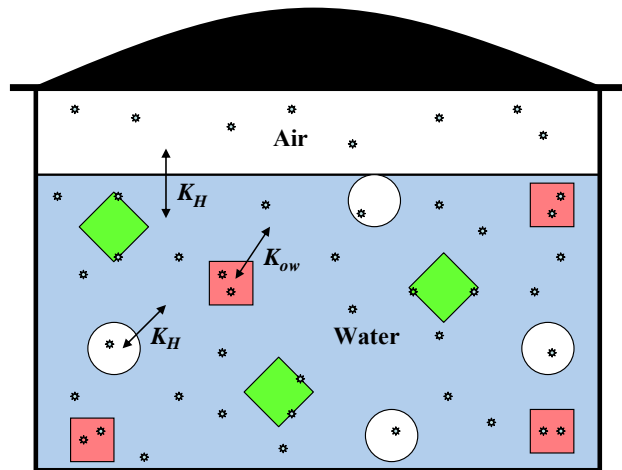


Figure 7: Simplified illustration of a meat stock in a closed pot. The meat stock consists of bulk water (blue) with dispersed oil droplets (□, red), proteins (◇, green) and vapour bubbles (○, white). Volatile compounds (∗) distribute between the oil, water and gas phase (air and vapour). In addition they bind to the proteins. In case of a low concentration of volatile compounds, the distribution of volatile compounds between phases at equilibrium is described by K_{ow} , the partition coefficients for oil/water, and K_H , Henry's law constant for gas/water.

Water-Gas distribution (Henry's law)

To begin with, the volatility in a two-phase, system consisting of only water and gas is considered. In the case where volatile compound is highly diluted the partitioning between water and gas phase, at a certain temperature, is described by Henry's law constant,

$$K_H = \frac{C_w}{p_g},$$

where C_w is the concentration of the compound in the water phase and p_g is the partial pressure of the compound in the gas phase. This law states that the amount of gas dissolved in a certain volume of liquid is directly proportional to the partial pressure of the vapour in equilibrium with the solution. In other words there is an equilibrium between the water and gas phase with regard to the volatile concentrations. The law is restricted to condition where the concentration of the volatiles are sufficiently low, and can be considered ideal dilute (the activity constant is 1). The concentration range in which Henry's law is obeyed varies with the volatile. In most foods these conditions are met and Henry's law can be used to predict the partitioning of a aroma compound between the water and gas phases (Taylor 1998). A compilation of Henry's law constants is given by Sander (1999).

The Henry's law constant is temperature dependent; an increase in temperature causes a decrease in K_H , meaning the volatility increases (Sander 1999). The polarity of a compound affects the volatility, the more polar compounds, being more hydrophilic are less volatile, meaning the K_H is higher. This is shown by (Covarrubias-Cervantes et al. 2005) who studied the solubility in water of some esters, alcohols, aldehydes and ketones in a two phase system. The results illustrated how the more lipophilic (less polar) esters are more volatile, whereas e.g. the more hydrophilic(polar) alcohols are less volatile.

Oil-water distribution (Nernst distribution law)

The volatility predicted from Henry's law will be lowered by partitioning of the compounds into the oil phase in the stock. This distribution of a compound between oil and water likewise results in a constant ratio of concentration between oil and water at equilibrium. This is expressed by Nernst Distribution law, which

states that when a solute (e.g. an aroma compound) is dissolved in a mixture of two immiscible solvents (e.g. water and oil), the solute distributes in the two solvents so that the ratio of solute concentrations in the two solvents is constant at constant temperature. This law also applies only to ideal dilute solutions. In the case of distribution between oil and water in a stock, the distribution constant is given as,

$$K_{ow} = \frac{C_o}{C_w},$$

where C_o and C_w are the concentrations in oil and water, respectively and K_{ow} is the Nernst distribution constant, which in this case more commonly is referred to as the oil-water distribution constant.

The distribution between the oil and water phase for a given compound is a measure of the lipophilicity of the compound which is related to its chemical structure (polarity). Since most aroma compounds are lipophilic (although the lipophilicity varies greatly) the presence of oil in food tends to have a significant (compound dependent) effect on aroma release into the air. Hydrophilic compounds are however less affected by changes of fat level compared to the lipophilic (Preininger 2006; Reineccius 2006).

The lipophilicity of a compound depends on the chain length, volatile compounds with long aliphatic chains are in general more lipophilic (less polar) than the short-chained ones. The higher the lipophilicity the less volatile because of the higher degree of partitioning into the oil phase. Hence the volatility in a three-phase system, such as a stock, depends not only on the distribution between water and gas as described by Henry's law but also on the partitioning into the oil phase described by the oil-water partition constant, K_{ow} (Nernst distribution constant).

Based on these considerations it can be expected that long-chained lipophilic volatile compounds are less likely to evaporate during stock preparation and that the evaporation will be affected by the amount of oil present. The amount of oil in a stock is usually rather small due to skimming of the stock. However, even a relatively small amount of oil may have a significant effect on the loss of the long-chained volatile compounds during cooking, as also discussed by This (2007e).

A study by Riéra et al. (2006) illustrates the effect of oil on the release of aroma compounds. They investigated the effect of oil and other macromolecules on retention of a number of aroma compounds (mostly aldehydes) in a stock-type model. They showed that fat (5 g/L) effectively reduced the aroma release and that the aroma retention was proportional to the octanol–water partition coefficient (equal to the K_{ow} , describing lipophilicity) of the compound. They further showed an effect of collagen (2.7 g/L), which retained a substantial amount (20%) of the aliphatic aldehydes. Thus the study suggests a considerable effect of fat and collagen on aroma release in a stock but it does not predict the effect upon boiling or simmering of a stock. The retention effect reported for collagen will be explained in the following section.

Interaction with protein (Scatchard equation)

In addition to the equilibrium distribution of the volatile compounds in the three phases, it is likely that some interactions with non-volatile compounds in the stock will occur, affecting the loss of aroma. The so-called 'binding' of aroma molecules to non-volatile compounds may retain aroma compounds from being lost upon cooking but will also make them unavailable for perception. The binding of several non-volatile compounds have been studied, mainly polysaccharides and proteins (Kinsella 1989; Overbosch et al. 1991; Preininger

2006). The binding effect of in particular proteins may be relevant to the loss of aroma in a meat stock. The interaction between proteins and volatile aroma compounds have been reviewed by Kim and Min (1989) and O'Neill (1996). Two types of binding between proteins and volatile aroma compounds can occur, irreversible or reversible where the latter allows release of the aroma upon consumption of the food. Reversible binding of alcohol, aldehydes and ketones by hydrophobic interaction have been reported, alcohols having the lowest and aldehydes the highest binding capacity. Within the same chemical group the hydrophobic binding capacity increases with increase in carbon-chain length (hydrophobicity). The binding also depends on the number of hydrophobic binding sites on the protein, which become more accessible during denaturation (Preininger 2006). This suggests that the denaturation of meat proteins upon cooking of a stock may increase the binding of aroma compounds. The reversible binding of aroma compounds obeys the Scatchard equation at equilibrium,

$$\frac{v}{L} = Kn - Kv,$$

which relates the number of moles of protein-bound ligand per mole of total protein (v), relative to the molar concentration of free ligand L , with the total number of independent binding sites on the protein, n , and the association constant, K . (O'Neill 1996).

Since the gelatine in a stock is believed to increase in concentration upon reduction, it may have an increasing effect on the volatility of aroma compounds as the stock is boiled down. Yet, according to the review by Preininger (2006), gelatine mostly affects the volatility of aroma compounds in food by reducing their release rates because of the increase in viscosity which will be explained on more detail in section 10.3.2.

Interaction with polyphenols

Another non-volatile compound that may bind aroma compounds in a stock are the polyphenols. This is particularly relevant when using red wine in stocks and sauces since red wine contains a considerable amount of polyphenols, as will be explained in more detail in chapter 12. Binding of aroma compounds to polyphenols has been investigated in the context of wine since it is an important issue with regard to the quality of red wine. Although this has been less investigated than aroma binding by proteins, studies have shown a binding effect of several wine phenolics (Dufour and Bayonove 1999; Jung et al. 2000). Interaction between proteins and polyphenols will be further described in section 12.2.2 in relation to precipitation of this complex.

Salting out

Another phenomenon that may affect the volatility of aroma compounds in the stock is the influence of salt. Salt binds water molecules which lead to increased release of volatile aroma compounds by changing the equilibrium between the water and gas phase. A decrease in available water molecules by addition of salt causes a shift in the equilibrium causing the more volatile compounds to diffuse into the gas phase. This increase in volatility caused by increase in salt concentration is referred to as 'salting out'. The effect of this phenomenon on volatile aroma compounds have among others been documented by Nawar (1971). It can be expected that this may affect the volatility of the aroma compounds in the stock particularly in the later stages of the reduction where the volume has been reduced and the salts have been concentrated.

10.3.2 Non-equilibrium conditions and diffusion

The general knowledge on physical chemistry presented above describes the ‘static equilibrium distribution’ but as explained by Preininger (2006) the ‘dynamic factor’ also influences flavour release. As already explained, partitioning between phases determines the volatility and ultimately retention and release of volatile compounds under equilibrium conditions. The volatility is compound-dependent and also dependent on the food matrix. When phase equilibrium is disturbed as for example when removing the lid from the stock pot, mass transport takes place from the bulk product to the surface in attempt to restore the equilibrium. The concentration gradient is the driving force for mass transport.

Diffusion is the mechanism by which components are transported by means of random molecular motion from regions with high concentration to those with a low concentration. The number of particles that diffuse through a unit area per unit time, the flux (J), is related to the concentration gradient (dc/dx) by Fick’s 1st law,

$$J = -D \frac{dc}{dx},$$

if the flow is one-dimensional (Dill and Bromberg 2003). D is the diffusion constant that describes the rate with which the particles diffuse. D is related to the temperature, viscosity of the fluid and the size of the particles according to the Stokes-Einstein relation, which says that small particles at raised temperature diffuse at a faster rate (Walstra 2003c). Fick’s law imply that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient. In more than one dimension the flux, J , is a vector (Dill and Bromberg 2003).

10.3.3 Aroma loss from a stock upon heating

What controls the loss of aroma compounds in a stock upon heating (cooking and reduction)? Can we predict the loss based on the equilibrium conditions, or is the loss controlled by the diffusion? Do the aroma compounds leave the stock mainly at the surface or more through the loss of vapour bubbles from the boiling or simmering stock? This remains to be investigated but based on the above theories and on suggestions by de Roos (2006), some explanations, related to aroma loss in an open pot, are proposed.

De Roos (2006) suggested that aroma loss from a static liquid (no convection) is likely to be diffusion-controlled because the mass transport is relatively slow. A slow mass transport will lead to a higher depletion of the aroma compounds at the and correspondingly a higher chance that the release will be controlled by the rate of transport to the surface as opposed to the volatility of the compound at equilibrium (de Roos 2006). This is illustrated in a meat stock model, Figure 8a. In such case, compounds with a high volatility will be depleted at the surface of the stock to a larger extent and thereby increase the driving force for mass transport from the bulk of the stock to the surface. When the concentration gradient is at its maximum (surface concentration of the product close to zero), the release of volatile compounds from the stock will be completely controlled by the rate of mass transfer taking place from the bulk to the surface in order to restore the equilibrium. In case the loss is entirely controlled by mass transfer, then the rate of evaporation will be independent of the individual volatility of the compound (de Roos 2006) but dependent on the rate of diffusion, as describes by Fick’s 1st law. Since the diffusivity constant, D , is dependent on viscosity of the fluid, the rate of mass transport is influenced by the viscosity of the stock (Bakker et al. 1998; Preininger 2006) but does not change much with aroma compound (de Roos 2006). Thus in case the aroma evaporation

is diffusion-controlled the loss can be assumed to be independent of aroma compound but dependent on viscosity of the stock. In such cases the increase in viscosity upon reduction, associated with the concentration of gelatine, will cause a decrease in aroma release as already described in section 10.3.1.

The opposite situation is argued by de Roos (2006) to hold for a turbulent boiling liquid. In this case the loss of volatile compounds is suggested not to be controlled by diffusive mass transport since the vapour bubbling upwards ensures an effective mass transport. Therefore the vapour phase concentrations of the vapour bubbles can be assumed to be close to those at equilibrium, and hence controlled by the described equilibrium conditions. If the vapour bubbles leaving the stock are in equilibrium with the volatile concentration of the bulk food, the loss of volatile aroma compound will be dependent on the amount of water evaporated (de Roos 2006), if neglecting the loss through the surface of the stock. The concentration of the bulk stock is of course constantly decreasing and hence the equilibrium concentrations change accordingly. Figure 8b illustrates a turbulent boiling stock where an efficient mass transport throughout the stock ensures equilibrium distribution of the aroma molecules.

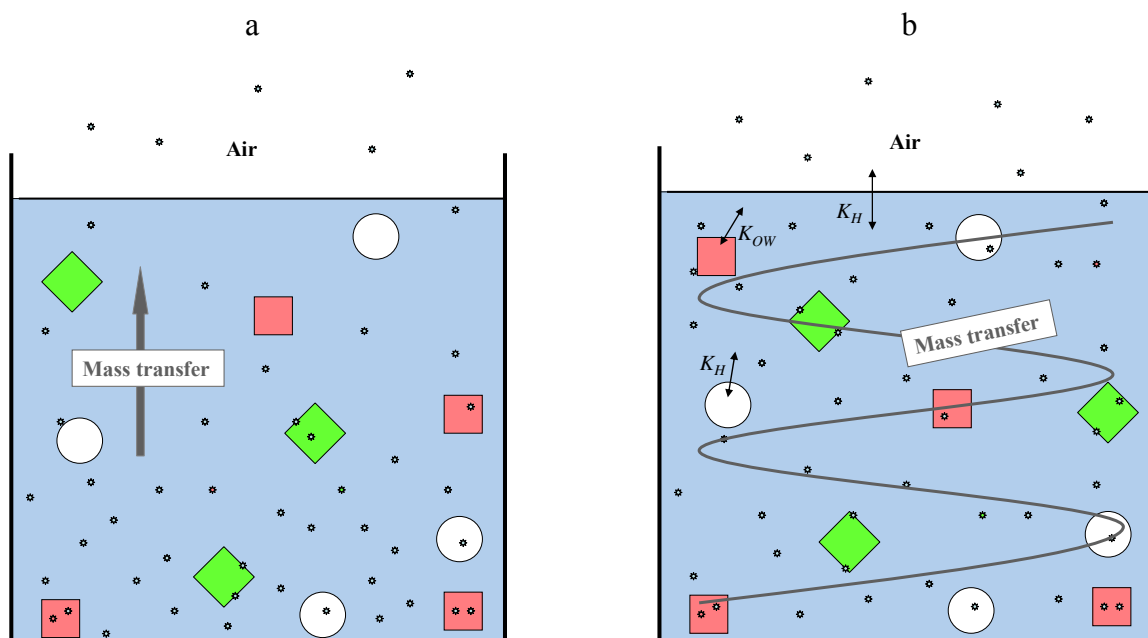


Figure 8: Simplified illustrations of a meat stock in an open pot. The meat stock consists of bulk water (blue) with dispersed oil droplets (\square , red), proteins (\diamond , green) and vapour bubbles (\circ , white). Volatile compounds (\ast) distribute between the oil, water and gas phase. The figure illustrates two hypothesised conditions upon cooking of meat stock, a) Static conditions: There is a depletion of the volatile compounds at the surface and mass transport takes place from the bottom to the surface, and b) Dynamic conditions: Due to the turbulence of the water created by boiling, there is an efficient mass transport through the water and the volatile phase concentrations are in equilibrium.

To which extent the loss of volatile aroma compounds during reduction of a stock in an open pot is diffusion-controlled or controlled by the volatility at equilibrium and amount of water evaporated has not been investigated. It is likely to depend on to which extent the stock is vigorously boiled or carefully simmered, where boiling probably favours control by equilibrium. In addition it can be assumed to depend on the viscosity of the stock, since the diffusion rate (and total flow of compounds as given by Fick's law) is slower in more viscous liquids. Thus increasing the viscosity by reduction causes a decrease in diffusion rate and a higher chance that the loss of volatile compounds is controlled by diffusion. The dimensions of the stock pot may also have an influence, at least in case of non-equilibrium conditions as illustrated in Figure 8a. The

taller the pot the smaller the concentration gradient from bottom to the surface and the longer the distance over which mass transfer must take place in order for the aroma compounds to reach the surface.

Assuming that the stock is boiling and there is an efficient mass transfer (hence not diffusion-controlled) as suggested by de Roos (2006), and thus there is an equilibrium between the phases in the stock as shown in Figure 8b, then the loss of volatile aroma compounds depends on the individual partition constants of the aroma compounds. In such a case loss of volatile aroma compounds from the stock to the surroundings can happen through diffusion at the surface and through the vapour bubbles leaving the stock. If the loss of volatile aroma compounds at the surface is neglected, then the loss of aroma will be proportional to the rate of water evaporation as bubbles. If the concentration of a volatile aroma compound (ratio of volatile compound to water) is higher in the vapour bubbles than in the surrounding stock (high volatility), evaporation will cause decrease in concentration of that compound in the stock and vice versa. Only in case of a very low volatility, however, will the evaporation of water result in an increasing stock concentration (eg. the 'non-volatile' taste compounds).

The complexity of food systems makes it very difficult to predict or measure the effect of the individual ingredients and it is even more complicated to predict the changes upon cooking. As illustrated above a stock is a liquid with several phases and compounds suspended/ dissolved/emulsified in it and various physical mechanisms are relevant to the conditions present upon reduction of stock. These theoretical considerations are applied in the discussion of the results obtained in Paper III and in identifying further relevant problems to be investigated with the purpose of increasing the insight into flavour retention upon cooking of stock and similar preparations in the kitchen.

11 REDUCTION OF MEAT STOCKS

Brown sauces are based on reduced stocks, which provide meat flavour and texture to the sauce (Peterson 2008). Reduce means to boil a liquid down (Sokolov 2007), which is done with stock and wine as a part of sauce preparation. The reduction of stocks has the purpose of increasing the viscosity and simultaneously increasing the taste and aroma intensity (McGee 2004c). Relevant problems regarding the stock reduction will be defined and discussed. The related study of flavour development, published in paper III, will be presented.

11.1 IDENTIFYING THE PROBLEMS

11.1.1 The aroma paradox

It is not complicated to understand how a concentration of the non-volatile taste compounds as well as gelatine may occur upon reduction of stock as a result of the decrease in volume by water evaporation. It is on the other hand an apparent paradox that when reducing stock or wine, volatile aroma compounds are boiled off as evidenced by the smell in the kitchen, but despite the loss of aroma compounds, the resulting wine or stock reduction has an intense aroma. This paradox is also identified by McGee (1999) and This (2006a) who call attention to the lack of scientific understanding of this culinary preparation. They further refer to the apparently un-published results from an experiment by A. Blake, Firmenich, Geneva who appears to have investigated the aroma paradox and found that while aromas are boiled off new aromas are formed during heat induced reactions. This (2006a) concludes that it remains to be identified which chemical reactions are important in flavour generation through a reduction. Moreover This (2007c) proposes to investigate the important chemical processes during very long treatments such as meat stock preparation. Vega and Ubbink (2008) likewise identify stock reduction as a basic kitchen process which is still unexplored by scientists and notice that 'almost nothing is known about the generation and degradation occurring during the reduction step' (Vega and Ubbink 2008).

The loss of aroma during cooking was observed and discussed already by Count Rumford (1753-1814), who strongly suggested to avoid vigorous boiling and instead prepare soups and other foods below the boiling point: 'It is natural to suppose that many of the finer and more volatile parts of food (those which are best calculated to act on the organs of taste) must be carried off with the steam when the boiling is violent; but the fact does not rest on those reasonings. It is proved to a demonstration, not only by the agreeable fragrance of the steam which rises from vessels in which meat is boiled, but also from the strong flavour and superior quality of soups which are prepared by a long process over a very gentle fire' (Rumford 1969).

This issue of aroma loss during cooking and reduction of a stock is also raised by This (2007e) who argues that since aroma molecules generally are lipophilic they should be most concentrated in the oil phase of the stock, which is usually removed by skimming and filtering of the stock or removed as a fat layer after cooling. In view of that This (2007e) raises the questions of how to keep the aromas in the stock during reduction and whether the aromas can avoid escaping when the stock only simmers.

Lack of understanding of the changes in flavour in a stock upon preparation and the possible effect of boiling versus simmering, was the starting point for the scientific investigation of how flavour develops through meat stock reduction with emphasis on the volatile aroma compounds (Paper III). The purpose of the study was to gain an increased insight into the chemical and physical matters during reduction, affecting flavour of the reduced stock. Paper III encompasses a study on the changes in volatile composition and perceived flavour upon reduction of meat stock and the effect of reduction rate.

11.1.2 Concentration factor versus reduction time

As already described in section 9.2.2, cookbooks often prescribe how far to boil the stock down and refer to a percentage of the initial volume that the stock should be reduced to, like 10% to obtain a glace (which corresponds to a 'concentration factor' of 10). On the other hand cookbooks generally do not pay much attention to reduction rate and accordingly the reduction time (Larousse 1993; Larousse 1997; Peterson 2008; Sokolov 2007; The Culinary Institute of America 2006). The advice on reducing to a certain percent of the initial volume is apparently related to getting the viscosity right, since the viscosity increases with a decrease in volume. In the sauce cookbook by Roux (1996) it is advised to 'reduce the sauce over high heat to obtain the desired consistency'. However, by varying the power input relative to batch size, the rate of reduction can be controlled and thus the reduction time to obtain a certain concentration factor is not fixed. In other words you can obtain the same concentration factor (and same viscosity) by means of either fast or slow reduction. Reduction time and concentration factor are obviously co-dependent factors but the rate of the reduction, controlled by the relative power input (heat per time per volume stock), determines the relationship between reduction time and concentration factor.

Cookbooks that give advice on stock preparation do not seem to recognize the difference and interrelationship between concentration factor and reduction time. In the rather profound discussion in the sauce cookbook by Peterson (2008) on the extent of reduction for obtaining the optimal glace, there is no clear distinction between time and concentration factor. Peterson (2008) thinks nevertheless that reduction can happen too slowly. He recommends to use a high gelatine stock for glace preparation since the reduction time otherwise will be too long for obtaining the desired texture which results in loss of flavour. He warns the chef not to 'overreduce' the stock, since 'many of the flavours in stocks are aromatic and evaporate when simmered over a prolonged period, leaving it flat in taste' and he suggests to add more fresh herbs and vegetables if the finished stock tastes flat. He also notices that compared to a glace, the loss of volatiles are diminished in a demi-glace, due to the shorter reduction time and not least, the very sticky consistency of the high gelatine glace is avoided (Peterson 2008).

Although the concentration factor, as advised on in cookbooks, may determine the concentration of gelatine which determines the viscosity it may not by itself determine the flavour. The effect of concentration factor relative to reduction time on the flavour has been studied in Paper III.

11.1.3 Assumptions and hypotheses

Prior to discussing the results of Paper III, some assumptions and hypotheses are presented. It seems reasonable to assume that the non-volatile gelatine will be concentrated during reduction, which explains the increase in viscosity as the stock is reduced. The same can be assumed to happen to several of the non-volatile taste components as sugars, nucleotides, salts, peptides and amino acids, which explain the

concentrated savoury flavour of the reduced stocks. Accordingly, Peterson (2008) makes a note of how the natural sugars in vegetables become concentrated during reduction. The popular science book on *Kitchen Science* (Hillman 2003) explains that ‘reduction does more than thicken. It concentrates existing flavours’. McGee (2004b) further supports this assumption by explaining how the reduced stock (meat glaze) has a concentrated savoury flavour due to the high concentration of for example amino acids, and is thick due to gelatine (concentration of app 25%).

McGee (2004b) moreover explains that although the many hours of simmering result in a very intense savoury flavour, it may seem rather ‘flat’ as a result of the loss of volatile molecules during the long cooking hours. Based on the theory on physical chemistry of flavour, as explained in section 10.3, it seems reasonable to assume that volatile compounds, at least to some degree, are boiled off during the hours- long reduction process. Regarding the loss of aroma, it can further be hypothesized that the oil present in the stock plays a role in retention of aroma upon reduction.

Furthermore it seems reasonable to assume that new aromas are formed during reduction, as also suggested by (McGee 1999) and (This 2006a), since applying heat to a solution/suspension of meat components will induce aroma generating reactions as explained in more detail in section 10.2.

11.2 EXPERIMENTAL STUDY OF BEEF STOCK REDUCTION

The experimental study published in paper III investigates the formation and decay of volatile compounds during reduction of a simple meat stock and the associated perceived flavour. It further studies the effect of concentration factor versus reduction time on the relative volatile concentrations and flavour intensity.

11.2.1 Experimental design

The study involves preparation of two large batches of meat stock (referred to as the Time experiment and the Power experiment) based on beef, water and sodium chloride only. Each of these was reduced according to Figure 9. After rediluting to the original volume, the (reduced) stock samples were analysed by gas chromatography (volatiles) and a descriptive sensory analysis (perceived flavour). Reduction of the first batch, the Time experiment (T), was done by reducing one large batch of stock for 22 h, taking out samples at different times during this period, as shown in Figure 9a. The second batch of stock, the Power experiment (P), was separated into four batches prior to reduction. Three of the four batches were reduced with various combinations of reduction time and concentration factor, as illustrated in Figure 9b. All reduced stock samples were rediluted prior to analyses.

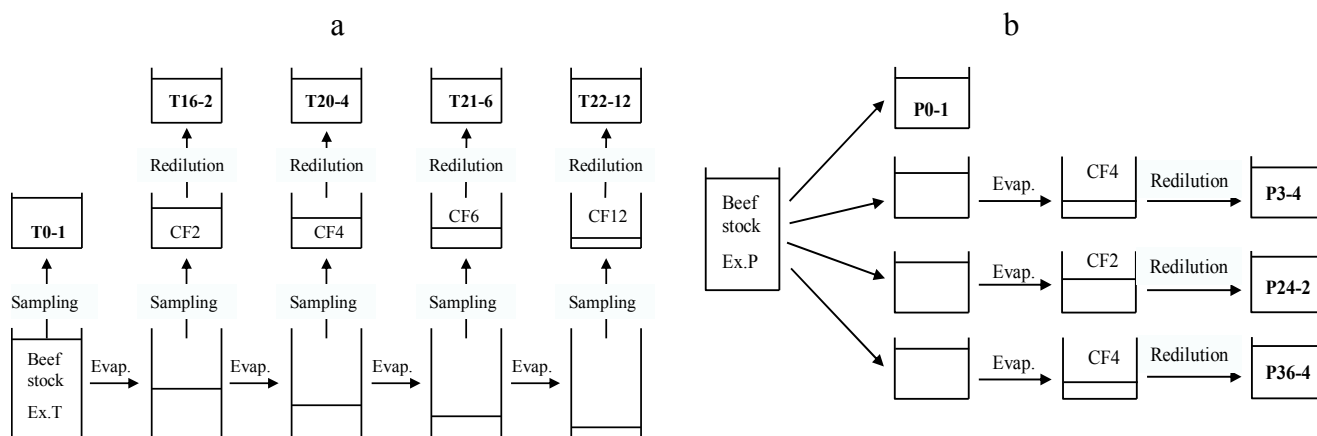


Figure 9: Experimental design of the study of flavour development during beef stock reduction (Paper III). The figure illustrates how the stocks were boiled down in a) experiment T (time) and b) experiment P (power). The resulting concentration factor (CF) is shown along with the sample names of the reduced stock samples. Sample names are constructed from a letter (T or P) referring to the experiment, a number referring to the reduction time (0-36 h) and a number referring to the concentration factor (0-12).

11.2.2 Effect of reduction time and power

Results from the Time experiment showed how perceived flavour changed in intensity during reduction and how volatile compounds could be divided into groups according to their progress in concentration with reduction time. In general some volatiles decreased with time, others peaked in concentration at some point during 16-20 h of reduction, and some increased with time. This is illustrated in Figure 10 which shows the outcome (scores and loadings) of a Principal Component Analysis (PCA) of the gas chromatography data in the Time experiment.

The increase in concentration of many volatile compounds, whether over the entire period or only to some point, confirms that there is an extensive generation of flavour in the stock during reduction. Since samples were rediluted to original volume before analysis, the increase can not be explained by a trivial concentration but must be explained by formation. Paper III speculates about the possible formation of the various compounds which is speculative. It is suggested that both oxidation, reduction, disproportionation and Maillard reactions take place.

The observed decrease in concentration of some volatile compounds is explained both by loss due to evaporation and by chemical break-down. It seems reasonable to assume that the loss of aroma from the simmering stock is at least not entirely diffusion controlled, which may have been the case in a static liquid as suggested by de Roos (2006). Most likely the situation in the stock upon reduction was somewhere in between the two hypothesized conditions in Figure 8. In such case the different volatile compounds in the stock are expected to evaporate at different rates depending on their volatility as described in section 10.3, which will change the relative concentrations of the volatile aroma compounds in the stock during reduction. The abundance of relatively long-chained aliphatic compounds detected in the reduced stock samples may be explained by retention of the compounds by oil present in the stock. The higher lipophilicity of long chained compounds increases their chance of retention by oil during reduction. This issue is also discussed by Ubbink (2010). He argues that the oil in a stock does not retain the important aroma compounds as could be expected. This is according to Ubbink (2010) evidenced by the lack of pleasant stock flavour when tasting

the oil removed from the stock during preparation. He further concludes that the desired volatile compounds must be mainly water-soluble. This remains to be systematically investigated, and so do the other factors that may control the loss of aroma upon cooking in an open pot.

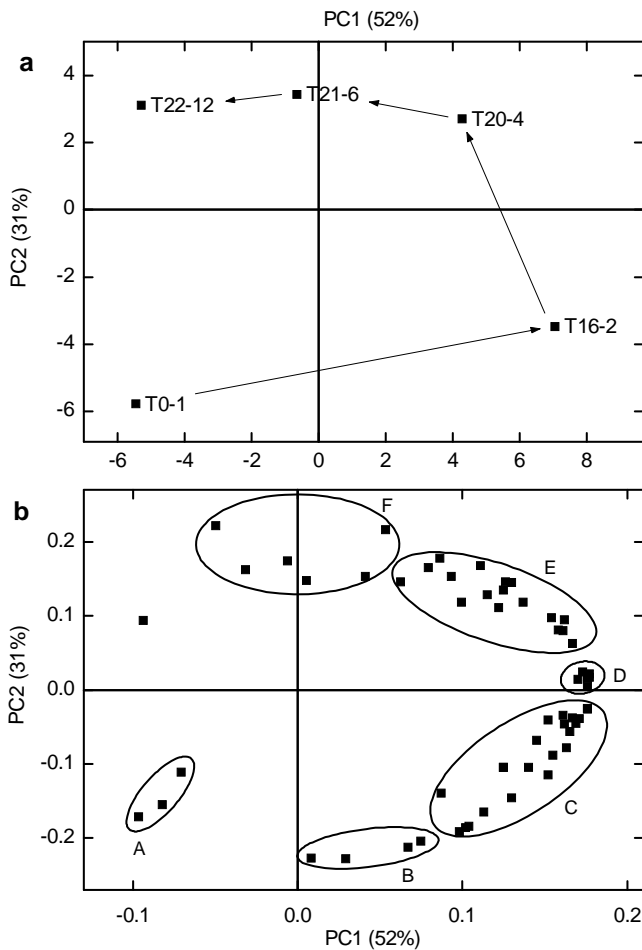


Figure 10: The outcome of a Principal Component Analysis on gas chromatography data on stock samples in Experiment T (Paper III). Scores (a) and loadings (b) of the first (PC1) and second (PC2) dimensions are shown, which describe 52% and 31% of the total variation in the data, respectively. Arrows in the scores-plot (a) illustrate the reduction. The position of the aroma compounds in the loadings-plot (b) are shown as dots and these are grouped (A, B, C, D, E and F) according to their progress in concentration upon reduction.

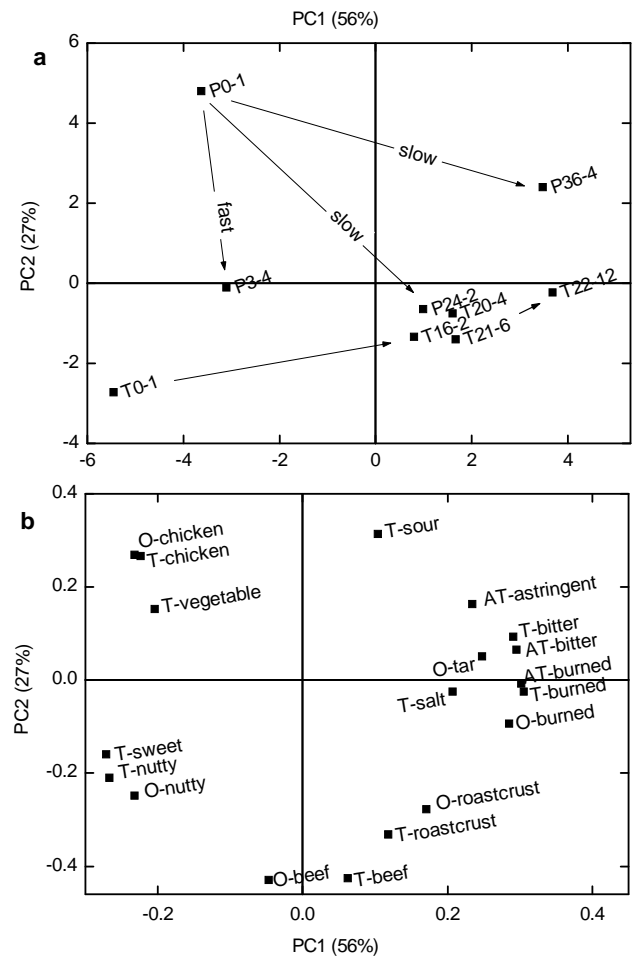


Figure 11: The outcome of a Principal Component Analysis on sensory data on reduced stock in Experiment T and P (Paper III). Scores (a) and loadings (b) of the first (PC1) and second (PC2) dimensions are shown, which describe 56% and 27% of the total variation in the data, respectively. Arrows in the scores-plot illustrate the reduction.

The sensory analysis revealed changes in perceived flavour with reduction time. Similar to the volatile compounds, some flavours decreased in intensity with time, others peaked at some point around 16 h, and some increased over the entire time period. Both of the experiments (Time and Power) showed that the initial boiled meat, vegetable and nutty flavour characteristics were lost while new flavour such as roast crust, burnt and bitter increased in intensity upon reduction. This is illustrated in Figure 11, showing the outcome (scores and loadings) of a Principal Component Analysis of sensory data for both experiments. In Figure 11a it is seen that the first dimension, PC1, represents the reduction time, meaning the long reduced stocks have high values on PC 1 and vice versa. The loading plot, Figure 11b, shows the related development in flavours

dependent on reduction time. These roasted and burned flavour notes are suggested to be further evidence of Maillard reactions. The loss of the initial perceived flavours is most likely related to the already mentioned decrease in concentration of several volatile compounds, but this particular relation was not investigated. Since the experiments only give limited data on the first hours of reduction, it also remains to be investigated how quickly the boiled meat and vegetable aroma are boiled off. The study shows however that the initial flavour is lost long before the increase in other flavours have reached their maximum intensities.

From the Time experiment there is evidence that by reducing too long (more than 16-20h) the reduced stock will be low in aroma since most volatiles decrease in the last hours of reduction. The sensory results further show that a very long reduction gives a very burned and bitter result. The taste compounds, for example the bitter peptides, are non-volatile and will only be more concentrated the longer the stock is simmering. In addition bitter compounds may be formed during the reduction.

The Power experiment studied the effect of power input from the stove which determines the rate of water evaporation during reduction. The results showed that by boiling a stock down to the same concentration factor (4) over a very short time (3 h) or a long time (36 h) respectively, controlled by the power input from the stove, gave very different flavour characteristics to the reduced stocks and correspondingly very different volatile profiles. The initial volatiles and the initial perceived flavours were lost in both cases but in case of the fast reduction (3 h) few new flavours developed, most likely due to the lack of time for the aroma-generating reactions. Based on an assumption about non-diffusion controlled conditions where the aroma loss happens mainly through the vapour bubbles leaving the stock (suggested in 10.3), the loss of aroma is independent of the time but dependent on the concentration factor. These results support that the decrease in initial aroma is independent of time but happens to the same degree in the fast and slowly reduced stock. However, since the development in volatile concentrations measured is the result of the combined effect of evaporation and formation of aroma compounds, more studies are needed to confirm or reject the hypothesis.

11.2.3 The practical outcome

The practical outcome of these experiments is that the chef should be more aware of the effect of reduction time versus concentration factor, the rate of the reduction. Cookbooks generally advise on the concentration factor but do not acknowledge the effect of reduction time independently. The concentration factor is believed to mainly determine the concentration of gelatine (viscosity) and non-volatile taste compounds (for example umami compounds) whereas the reduction time determines the formation of new aroma compounds (and possibly also non-volatile taste compounds) because of the time-dependent chemical reactions. The study generally shows a large effect of reduction time on the flavour, and hence the reduction time is an important factor to adjust when optimizing stock reduction. A lot of the initial flavours are lost within the first hours of reduction but on the other hand new flavours are formed with time. If both the initial boiled meat, vegetables and nutty flavours as well as the 'reduced flavour notes' are desired, it may be a solution to add fresh meat and vegetable toward the end of reduction.

Based on the result from these experiment no advice can be giving regarding the optimal time of reduction; it has only been shown that by adjusting the reduction time, the flavour varies considerable and hence the reduction time as relative to the concentration factor should be controlled in order to meet the desired stock flavour and texture. Hence it is beneficial for the chef to realize how the concentration factor and reduction

time both influence the final flavour of a reduced stock and how the relation between these two factors can be controlled. By controlling the rate of reduction (given by the power input relative to batch size) the relation between concentration factor and reduction time can be chosen. For the chef this means choosing the appropriate power input from the stove and amount of stock to be reduced in one batch.

Figure 12 shows a diagram of reduction time versus concentration factor. This diagram illustrates how different flavour characteristics of a reduced stock can be obtained depending on the reduction time relative to the concentration factor. By changing the rate of reduction different coordinates in the diagram can be obtained. The equipment available in the kitchen will of course limit the possible reduction rates of practical relevance and limit the chef's options for controlling flavour. The coordinates in the diagram, as determined by the concentration factor and the reduction time, are suggested to give a good indication on the final flavour properties. On one hand, the concentration factor by itself is assumed mainly to determine the texture and the savoury flavour caused by concentration of non-volatile taste compounds (eg. salts, nucleotides and amino acids). The concentration factor may also be an important factor determining the loss of volatiles upon reduction if aroma compounds are mainly lost as a result of the water evaporated, as previously discussed. On the other hand, the reduction time, as shown in both experiments, is a very important factor for the development of volatile compounds, because of the chemical reactions happening with time. Reduction time is likely also to be important to the further development of non-volatile taste compounds in the stock.

The figure illustrates the suggested results of varying the reduction time relative to the concentration factor. The proposed flavour development, as illustrated in the figure, is based on the results obtained in Paper III as well as some assumptions on the effect of reducing the volume by boiling off water. The figure shows how a high concentration factor leads to a high concentration of gelatine and taste compounds, thus a glace (CF of 10) is a highly viscous liquid with an intense savoury flavour. The reduction time, however, further influences the flavour. A fast reduction with a high power input relative to batch size results in a reduced stock low in aroma, explained by the lack of time for formation of aromas. By reducing somewhat more slowly the resulting reduced stock will have a higher concentration of aroma compounds, probably due to the longer time for chemical reactions leading to formation of new compounds. Nevertheless the Time experiment also showed that the general increase in concentration observed continues only to a certain point (16-20 h in the Time experiment) after which several aroma compounds decrease in concentration. Although more precise advice cannot be given based on the current knowledge, the figure suggests that the reduction rate can be too high, due to the quick loss of aroma. On the other hand the reduction time may also be too long due to the observed decay in concentration of several volatile compounds observed.

Although it may be convenient and useful to think of flavour formation upon stock reduction in this way, the truth is without doubt more complicated. The formation of new aroma compounds also depends on the concentration factor since the reactant concentration affects the rate of chemical reactions leading to flavour. The two-dimensional illustration is however suggested as a simple picture to support and interpretation of the results, and to illustrate how the flavour and mouthfeel can be altered by controlling the concentration factor and the reduction time.

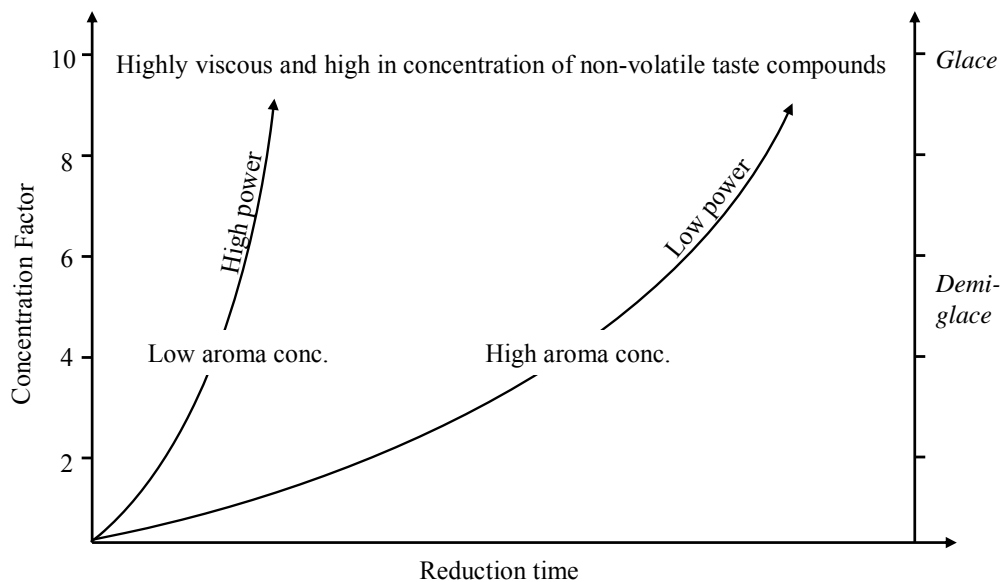


Figure 12: Diagram of reduction time versus concentration factor, showing the effect of these factors on flavour upon reduction (boiling down) of a stock. The figure is based on the discussion of results obtained in Paper III (*Flavour development during beef stock reduction*). Generally, the higher the concentration factor, the higher the concentration of non-volatile taste compounds as well as gelatine. A so-called *glace* is obtained by reducing to a concentration factor of approximately 10 (10% of initial volume). The flavour development upon stock reduction is however further influenced by the reduction rate (relative power input) which can be controlled by adjusting the power input relative to batch size. A high reduction rate, which corresponds to a high power input upon reduction, is seen to result in low aroma concentration whereas a lower reduction rate, obtained by a lower power input, results in a higher aroma concentration. This is explained by the great formation of aroma compounds happening with reduction time.

In case of routine operations in the kitchen with a consistent and non-flexible batch size and power input, the rate of reduction will be fixed (corresponding to a fixed slope in the diagram) which will decrease the possible flavour outcomes of the reduction. When deviating from a standard procedure it is on the other hand particularly important to be aware of how the flavour changes with reduction time, even if the concentration factor is maintained according to a recipe.

Another related observation from this study is that when reducing two initial different batches of stock, the initial differences in perceived flavour as well as volatile composition decrease with time. In other words, the longer the stock is reduced the less important the initial flavours of the stock are to the final result.

12 USING RED WINE IN STOCKS AND SAUCES

Stock reduction, as discussed in chapter 11, is a crucial step toward preparation of a classic brown sauce. This chapter examines the use of red wine in stocks and sauces, and takes one step further toward a classic French sauce made of reduced meat stock and red wine. The examination of the use of red wine in meat stocks is moreover relevant to a more general understanding of the use of wine as an ingredient in cooking. Wine is not only an ingredient in a variety of sauces but can also be used as an ingredient in other dishes like stews and soups. Several cookbooks on cooking with wine have been published (Ballard 1998; Goldstein 2004; Hoffman and Hoffman 1997; Weir 2001).

In this chapter the basic steps in preparation of stock-based brown sauces containing red wine are presented, followed by an identification of and elaboration on the related problems, and finally a presentation and discussion of Paper IV (*Beef stock reduction with red wine, effect of preparation method and wine characteristics*).

12.1 PREPARATION OF STOCK-BASED BROWN SAUCES

According to the systematic categorization of French sauces introduced by Carême and Escoffier in the 19th and 20th century, brown sauce, which is based on reduced brown stock, is one of the four basic sauce families. The large number of derivative brown sauces are made by adding a basic *flavour element* to the reduced stock (possibly a demi-glace which has been thickened further with starch). The stock can then be further reduced, strained and finished with e.g. butter, herbs and essences. In this way a large number of sauces can be made in a short time if a reduced stock is at hand (Peterson 2008). The basic steps in preparation of the stock-based brown sauces are illustrated in Figure 13.

Often the basic flavour element is made by reducing (boiling down) wine with other ingredients like onions and herbs. The so-called ‘red wine reductions’ are a common ingredient in the classical French sauce kitchen. It is often recommended to reduce the wine by half or three-fourths (corresponding to concentration factor of 2-4). Wine can also be used to deglaze⁹ the pan during stock preparation and in this way add flavour to the sauce (Escoffier 1979; Larousse 1993; Peterson 2008; The Culinary Institute of America 2006).

⁹ adding liquid to the roasting pan in order to dissolve the deposits

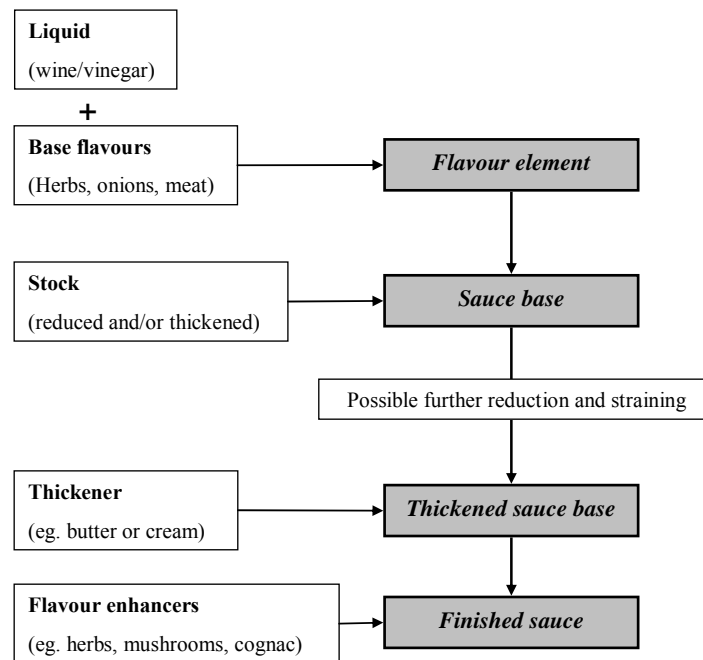


Figure 13: Basic steps in preparation of a stock-based brown sauce according to Peterson (2008)

12.2 IDENTIFYING THE PROBLEMS

Two main topics related to the use of red wine in beef stocks and sauces are examined. These are the choice of wine and the possible interaction of wine phenolics (tannins) and meat proteins when combined in a stock pot. First cookbook prescriptions on these matters are studied and then the relevant scientific literature is presented. Subsequently the scientific investigation of these matters (Paper IV) is presented.

12.2.1 Choice of wine

Choosing the appropriate wine for cooking, in particular sauces and stocks, is discussed by Peterson (2008). He advises that wines for cooking must be chosen on different criteria than wines for drinking since wine is 'radically transformed by heat and other aspects of the cooking process'. Peterson (2008) further advises not to use great wines for cooking since 'the finesse and complexity of such wines are destroyed by heat'. He moreover suggests not to choose lightly coloured fruity red wines because 'the delicate fruitiness that makes these wines charming to drink will be lost'. The better wines for sauce making are according to Peterson (2008) deeply coloured low acid wines, for example wines from hot climates or those made from early-ripening grapes such as Merlot. The wines are recommended to have been aged several years in the bottle in order to ensure that the 'flavours are well developed' and that 'the tannins have fallen out'. He moreover suggests that a 'certain amount of oakiness is also welcome' and also recommends to use California Zinfandel or Rioja (Peterson 2008).

Recommendations by other cookbook authors are much less detailed. Larousse (1993;1997) specifies that the red wine must be 'dry' and argue that the wine acidity aids the clarification process. Beck et al. (1978) states that 'any wine or spirit used in cooking must be a good one. If it is excessively fruity, sour, or unsavoury in any way, these tastes will only be emphasized by the cooking, which ordinarily reduces volume and

concentrates flavour'. Hillman (2003) and Corriher (1997) emphasize that the wine must be of 'drinking' quality and advise against the use of red wine labelled 'cooking wines'. Goldstein (2004) just advises not to use inferior quality wines.

The study on beef stock reduction with red wine, Paper IV, looks into the effect on flavour depending of the choice of red wine. In order to understand the possible effects of choosing one wine as opposed to the other, it is useful to briefly review the main flavour molecules present in red wine.

Red wine obtains its taste and mouthfeel from the content of sugars, acids, phenolics and ethanol. Ethanol in wine is important to the so-called 'body' of a wine, which is a mouthfeel sensation¹⁰. It moreover has an effect on the perception of other flavour compounds. The sugars (fructose and glucose) contribute sweetness and body to the wine. Wines that have a low sugar concentration (below 0.2%) are often described as 'dry'. Sugars can moreover diminish the harsh flavour sensation of wines which are excessively acidic, bitter and astringent. The organic acids in wine (the major one is tartaric) are essential to the refreshing or sour taste (tartness) of the wine. The acids further modify the perception of other compounds, for example they diminish the sweetness of the sugars (Jackson 2002).

The polyphenols contribute bitterness and astringency and this has been comprehensively studied (Arnold et al. 1980; Brossaud et al. 2001; Noble 1990;1999). The phenolic composition of wine consist of flavonoid and nonflavonoid monomers. The flavanoid monomers include flavanols such as quercetin, anthocyanins such as malvidin and flavan-3-ols such as catechin. The nonflavonoid monomers include e.g. caffeic acid, gallic acid, as well as the volatile phenolic aroma compounds such as benzaldehyde (Singleton 1988). The chemical composition of four phenolic compounds in wine are illustrated in Figure 14.

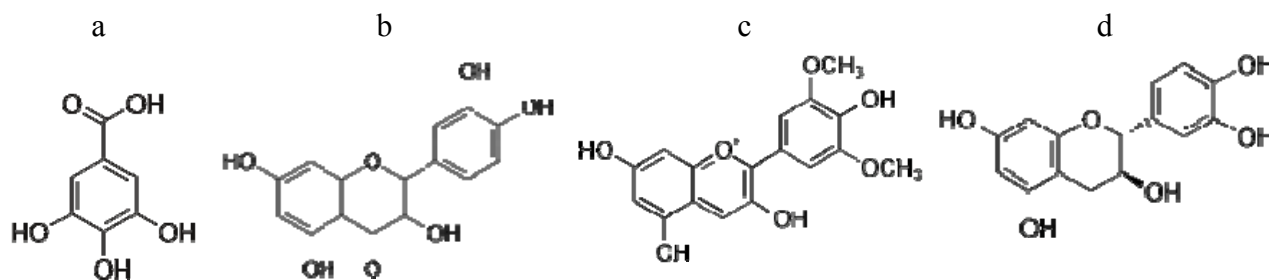


Figure 14: Chemical structure of one nonflavonoid (a) and three flavonoids (b, c and d), all common phenolic compounds in wine. Gallic acid (a), Quercetin, a flavanol (b), Malvidin, an anthocyanin (c) and Catechin, a flavan-3-ol (d).

The large group of polyphenolic polymers generated from these monomers are generally referred to as tannins. The flavonoid tannins constitute the major phenolic compounds in red wine. The polyphenolic concentration can vary considerably depending on grape variety and processing conditions (Ebeler 2001).

¹⁰ *Body* is a sensory term used to describe a mouthfeel sensation induced primarily by alcohol but also influenced by the presence sugars and phenolics. *Full-bodied* is a positive perception of 'weight' in the mouth, and the opposite (when *body* is lacking) is described as *watery* (Jackson 2002).

Monomeric polyphenols such as catechin, are generally considered to be more bitter than astringent while polymeric tannins are highly astringent (Arnold et al. 1980; Lea and Arnold 1978). Very large polymers, which may be formed upon storage, are not detected by the taste receptors and this is a common explanation for the decrease in astringency and bitterness upon aging (Jackson 2002).

The odour of wine is the result of a large range of volatile aroma compounds. These originate either from the grape (e.g. monoterpenes), the fermentation (e.g. alcohols and esters) or post-fermentation treatments such as oak storage (e.g. lactone). More details on the aroma compounds in wine are given in the review by Ebeler (2001).

A wine's concentration of non-volatile and volatile flavour compounds is dependent on grape variety, production methods and storage conditions. The concentrations of flavour compounds in a wine define the overall sensory characteristics of the wine. The influence of red wine characteristics on the flavour of a reduced wine and on a reduced stock with red wine is investigated in Paper IV.

12.2.2 Possible protein-tannin interactions

Sauces that call for red wine are typically made by reducing the wine and then mixing with reduced stock. The mixture may then be further reduced and finished with butter or cream as described in Figure 13. According to the sauce cookbook by Peterson (2008) and wine cookbook by Goldstein (2004) the problem with using reduced red wine in preparation of sauces is that the tannins and acids in the wine are concentrated which makes the sauce harsh. Peterson (2008) suggests that this problem can be alleviated somewhat by cooking wine together with the stock because the proteins from the stock will 'clarify out some of the tannins'. Peterson (2008) describes that 'when cooked with foods that contain protein, such as fish or meat, the tannins and pigments contained in the wine combine with the proteins that are released during cooking. This removes much of the colour, acidity and any astringency due to the tannin'. Hence reducing wine by itself or without any protein source gives a very different result than with a protein-containing food (Peterson 2008).

Peterson (2008) thus recommends to prepare a meat stock with red wine by cooking and reducing the wine together with the stock. It is however more convenient for the chef to make the reduced stock and the reduced wine separately; in this way he can rely on one basic stock reduction for a very large variety of brown sauces. Preparing the red wine reduction by itself and mixing with reduced stock is thus convenient but this common procedure will according to Peterson (2008) easily result in an astringent, bitter and sour sauce. On the other hand most classic recipes call for a second reduction with reduced stock and wine combined, which may be sufficient to the so-called 'tannin clarification'. Peterson (2008) suggests minimum 30 min of combined cooking time in order for this to happen.

The same issue is raised in the wine cookbook by Goldstein (2004) who likewise recommends to cook the red wine with the stock for minimum 30 min in order to reduce the astringency from the tannins, when preparing a sauce. McGee (2004b) also recognises this issue and suggests that the tannins from the red wine may be a problem since they, when concentrated in the reduced wine or reduced stock with wine, will become very astringent. McGee (2004b) further suggests that this problem can be avoided by cooking the wine down with protein-rich ingredient like meat stock.

Precipitation of wine tannins with proteins in meat stock has not been investigated scientifically but the interaction of proteins and polyphenols have been studied in other contexts. Precipitation of tannin with proteins is a common method for measuring the concentration of tannins in red wine, and has shown to correspond well to perceived astringency (Kennedy et al. 2006). The astringent mouthfeel, as already briefly explained in section 10.1.1, is generally believed to be the consequence of an interaction between polyphenols and salivary proteins which has received a great deal of attention by scientists (Pascal et al. 2009; Zanchi et al. 2008). There are however also evidence that astringency is a taste sensation (Bajec and Pickering 2008).

Precipitation of tannins by proteins is also used in clarification of wine, the so-called *fining*. The principles of this clarification method is similar to those of the traditional stock clarification method, described in section 9.2.3, which involves precipitation of cloudy particles by egg white proteins. A common fining agent in the wine industry is gelatine (Kolpan et al. 2002). Maury et al. (2001) investigated the effect of fining with gelatine and reported that the more polymerized polyphenolic compounds (the more astringent) were selectively precipitated by the gelatine and they further suggested that this may reduce astringency of the wine.

The interaction of protein with polyphenols has also been investigated in relation to haze in beer and other beverages. It is generally believed that such hazes are formed by the gradual polymerisation of simple phenols and the subsequent reaction of these polymers with proteins by which insoluble complexes are formed. Studies have shown that the principal component of such haze is proteins and polymeric polyphenols, though carbohydrates are also identified in the haze (Siebert 2006). Insoluble deposits formed in alcoholic beverages of the 'bitter' type (e.g. Gammel Dansk) have likewise been shown to be formed by polymerization of polyphenols followed by precipitation of these with proteins and carbohydrates (Refsgaard et al. 1996).

The mechanisms behind precipitation of protein and phenolic compounds are reviewed by Haslam (1988). The two main mechanisms suggested are 1) at low protein concentration, the polyphenols associate at one or more sites on the protein's surface and form a monolayer around the protein which is less hydrophilic than the protein itself which causes aggregation and precipitation, and 2) at high protein concentration, complexation of proteins and polyphenols through cross linking of proteins by the multidentate polyphenols.

Based on the existing literature, it is plausible that cooking of wine and meat stock could cause precipitation of wine phenolics and meat proteins. This is discussed further in Paper IV (presented below), which investigates the effect on flavour of cooking red wine together with beef stock, as recommended by Peterson (2008), versus preparation of wine and beef stock reduction separately.

12.3 EXPERIMENTAL STUDY OF BEEF STOCK REDUCTION WITH RED WINE

In order to advise on the choice of wine for cooking, one must know how cooking affects the wine; how the flavours change upon heating, and accordingly which flavour characteristics are important when choosing a wine for cooking. The study on beef stock with red wine, Paper IV, takes the first step towards an increased scientific knowledge on this topic by investigating how different flavour characteristics of two wines (a

Zinfandel and a Cabernet Sauvignon, chosen due to their apparent difference in tannin concentration) affect the flavour of the corresponding reduced wines (as prepared for use in a brown sauce) and further how it affects the flavour of reduced beef stock containing these wines. It is not intended to make any general recommendations to which grape variety to use for cooking, but instead to study how the initial characteristics affect the cooked dish. The study further investigates the effect of reducing the beef stock *together* with red wine as opposed to preparation of reduced wine and reduced stock *separately* and then mixing. As introduced above, cooking stock and wine together is suggested to have a great effect on flavour due to protein-tannin interaction.

12.3.1 Experimental design

The experimental design is shown in Figure 15.

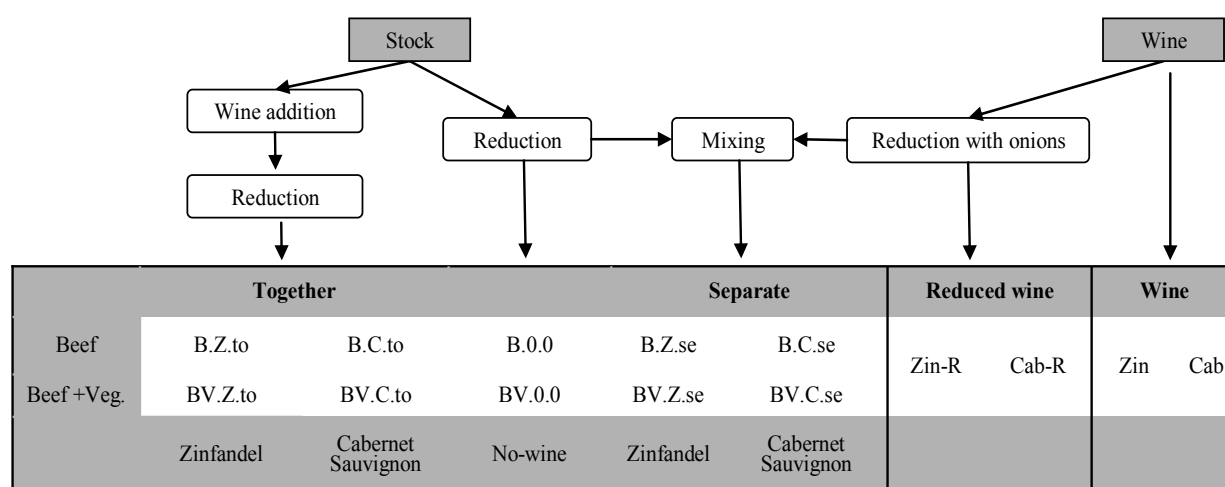


Figure 15: Experimental design of the study on beef stock reduction with red wine (Paper IV). The figure illustrates the preparation of ten different reduced beef stocks samples of which eight contained wine. Two different stocks were used, with beef only (B) and with beef + vegetable (BV). Two different red wines were used, a Cabernet Sauvignon (C) and a Zinfandel (Z). The reduced stock samples were prepared either without wine, or by reducing (boiling down) stock together (to) with red wine or by reducing wine and stock separately (se) and then mixing. Sample names are composed accordingly.

In brief, one large batch of beef stock was prepared according to a standard procedure. A sub batch of the strained stock was reduced by itself, another sub-batch reduced together with red wine and a third sub-batch reduced by itself but after reduction mixed with reduced wine. By using two different wines (Zinfandel and Cabernet Sauvignon) and by repeating the experimental setup with a beef stock prepared according to a simplified recipe (beef, bones and water only) a total of ten reduced stock samples were prepared of which eight contained red wine. In addition a sample of the two red wines and the corresponding red wine reductions were taken. All samples (ten reduced stocks, two reduced wines and two wines) were analysed by a sensory panel (descriptive sensory analysis) and by gas chromatography (volatiles). In addition the concentrations of sugars, acids and phenolics in the wines and reduced wines were analysed by HPLC according to a standard wine procedure.

12.3.2 Effect of wine characteristics

The results showed that the sensory panel could distinguish between reduced stocks and reduced wine samples made from Zinfandel and Cabernet Sauvignon, respectively. Results on the reduced stock samples

with wine can be seen in Figure 16, which shows the outcome of a PCA on the sensory data. It can be seen how the eight stock samples containing red wine are separated according to the wine (*Zinfandel* vs. *Cabernet Sauvignon*) used on the second principal component (PC2). Likewise, the relative volatile concentrations of the reduced stocks with wine could be separated by means of a PCA according to the wine used (PC 2 and 3), regardless of the reduction method, as shown in Figure 17b. In other words the initial differences between Zinfandel and Cabernet Sauvignon had a pronounced effect on the perceived flavour and on volatile composition of the reduced wines and reduced stocks with wine. By comparing the volatile concentrations in the red wine versus the wine reductions (red wine boiled down with onions), it is seen that many of the initial aroma compounds in the wine, for example the esters known to have a fruity aroma, are lost upon the reduction, while several new compounds are formed. Since many of the initial volatile aroma compounds from the wines were lost upon cooking or at least decreased considerably in concentration, the study concludes that the non-volatile composition of the wines is more important when choosing a wine for cooking. The non-volatile compounds are assumed to be precursors to formation of volatile compounds during the heating process and hence indirectly important to the wine-dependent aroma differences in wine and stock reductions.

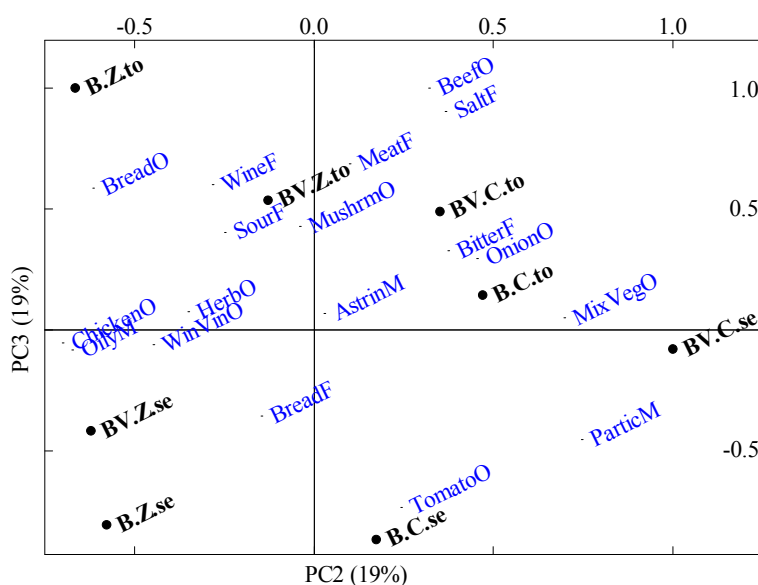


Figure 16: The outcome of a Principal Component Analysis on sensory data of the eight stocks samples containing red wine (paper IV). Scores (black) and loadings (blue) for the second (PC2) and third (PC3) dimension are shown, which describe 19% and 19% of the total variation in the data, respectively.

The concentration of non-volatile components was found to increase upon reduction of the wine with onions which is explained by their non-volatile nature. Accordingly, the Cabernet Sauvignon, which was perceived most bitter and astringent, was also the most bitter and astringent in the wine reductions. The higher bitterness was also perceived in the complete reduced stock with Cabernet Sauvignon as opposed to the reduced stock with Zinfandel. It is well known that phenolic compounds (tannins) have a bitter and astringent flavour. The concentration of these are presumably responsible to the high intensity of bitterness and astringency perceived in reduced wines and stocks with wine made from Cabernet Sauvignon. A study by Harbetson et al. (2008) showed that Cabernet Sauvignon had the highest tannin concentration compared to other common red wine grapes (e.g. Zinfandel). They investigated the variability in tannin concentration depending on grape variety by comparing 1325 commercial red wines based on five different grapes from

US, Australia and France. The results showed that there were significant differences among the varieties, Cabernet Sauvignon having the highest concentration. Thus a higher concentration of tannins in Cabernet Sauvignon was expected in this study but this was not confirmed by the HPLC analysis of the wines which showed higher concentration of some phenolic compounds in Zinfandel. The HPLC analysis is however limited to only a few phenolic compounds and has not been optimized in order to measure the complete content of tannins.

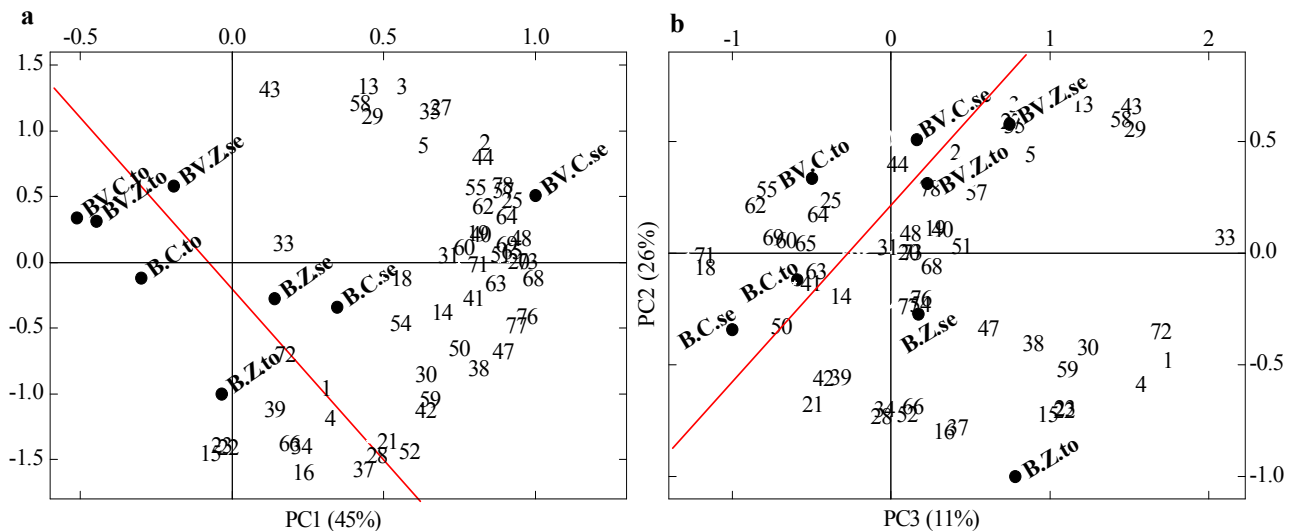


Figure 17: The outcome of a Principal Component Analysis on gas chromatography data of the eight stocks samples containing red wine (Paper IV). Scores and loadings in three dimensions are shown: PC1 vs. PC2 (a) and PC3 vs. PC2 (b), describing 45%, 26% and 11% of the total variation in the data, respectively. The red lines indicate the separation between stock samples according to reduction method, *separate* vs. *together* (a) and Zinfandel vs. *Cabernet Sauvignon* (b), respectively.

Due to the complexity of the stock, like any other food system, the formation of flavours upon cooking is very difficult to predict. Results from this study showed that the volatile compounds of the wine, for example the esters, decrease in concentration to a large extent upon cooking and hence the initial aroma of a wine is most likely not to be present in a perceptible concentration after cooking, which supports that great wines with an appreciated aroma should be kept for drinking. The study on the other hand suggested that the content of non-volatile taste compounds will greatly affect the flavour development, both due to increase in concentration of such compounds upon evaporation of water and due to the assumed chemical reaction leading to formation of new volatile aroma compounds with time. Hence the choice of wine for stock preparation and possibly other dishes should be based on taste and mouthfeel (sweetness, sourness, bitterness and astringency) of the wine. Yet, astringency might be less important if the wine and stock is heated together, which will be discussed further below.

These result confirm some of the advices given by the cookbooks, examined in section 12.2.1. Generally cookbooks agree that the choice of wine matters and inferior quality wines are not recommended. Beck et al. (1978) further argues that the flavours of the wine are emphasized after cooking, which according to the results from the present study, is only true for the taste and mouthfeel sensations. Peterson (2008) on the other hand recommends in accordance with our results that any fruitiness in a wine will be lost whereas the degree of acidity and tannin concentration is important. Based on the present study the optimal

concentrations of non-volatile compounds contributing to taste and mouthfeel can not be concluded but this could be a topic for further investigation in the field.

The results further show that precipitation of phenolic compounds with proteins, as suggested by McGee (2004b) and Peterson (2008), may likely have taken place. Stock reductions made with the more bitter and astringent Cabernet Sauvignon had a higher intensity of particulate mouthfeel which may possibly be the results of more protein-phenolic precipitation. This may then further explain that the higher initial astringency in Cabernet Sauvignon, as also found in the reduced wines with Cabernet Sauvignon, is not present in the stock reductions with wine. In other words, precipitation of astringent phenolic compounds during preparation of stock reductions with wine may simultaneously have caused the rise of particulate mouthfeel and decrease in astringency as suggested by Goldstein (2004) and Peterson (2008). The possible precipitation of phenolic compounds and proteins is further discussed below.

12.3.3 Effect of reduction method

The experimental study was further designed to study the effect of reduction method on the volatile aroma concentrations and perceived flavour in reduced stock samples with red wine. The results showed that the eight stock samples containing red wine could be distinguished according to the method used (reducing separately vs. together) by the sensory panel, regardless of which wine had been used. This is shown in Figure 16, where the stock samples are separated according to reduction method on PC3. Likewise, the stock samples could be separated according to reduction method by a PCA on the relative volatile concentrations, as seen in Figure 17a (PC1 and PC2).

Contrary of what was expected at the outset, there was a significantly ($p < 0.01$) higher intensity of particulate mouthfeel¹¹ in reduced stocks with wine prepared by reducing separately. The precipitation observed in stocks prepared by reducing separately is suggested to be the result of precipitation of tannins and protein, happening when the samples were heated prior to sensory analysis. The lower intensity of particulate mouthfeel in the stock reduced together with red wine is explained by the fact that the stocks were filtered before sensory analysis and possible precipitate formed during reduction had been removed by filtration before sensory analysis. Thus this study suggest that heating of stock and wine for max 45 min (as done prior to sensory analysis) is enough for the precipitation to take place. The results further suggest that such precipitation can reduce the final astringency in the reduced stock when prepared from a highly astringent wine.

The interpretation of the results is strongly based on the hypothesis generated from the cookbooks as well as the scientific literature presented in section 12.2.2. The experimental study conducted on beef stock reductions with red wine was however not designed particularly to study the interaction between proteins and polyphenols, and therefore no definite conclusion to whether this has happened or not can be drawn based on the results obtained. Further investigation is needed to confirm whether precipitation of phenolics and proteins happens when cooking stock and wine, and what effect it may have on the perceived flavour as suggested by several cookbook authors. Another suggestion from a cookbook author (Larousse 1993) is that the wine acids aid the clarification process (clarification of stocks is described in section 9.2.3), and thus that

¹¹ The feeling of particles or grittiness in the mouth.

the acids are essential in precipitation of proteins. This postulate by Larousse (1993) could also be investigated.

Apart from mouthfeel and astringency, the two different reduction methods (reducing separately vs. together) were shown to cause more differences in the perceived flavour as well as the volatile composition. For example, the beef odour intensity was significantly higher when reducing together. No precise explanations for these general differences according to methods are given, but considering the complex reactions and interactions in a stock upon heating, which depends on the initial concentration of precursors, large variation in taste and odour must be expected. The variation observed in the final flavour characteristics is assumed to be a result of the difference in initial composition possibly combined with an effect of a difference in pH (depending on wine addition) upon cooking.

Based on these results it is concluded that choice of wine is important for the flavour of the reduced stock with red wine, and that it is the wine's content of non-volatiles which are of greatest importance because initial aroma is lost due to evaporation. Although red wines from two different grape varieties were investigated, the study does not attempt to make any generalisation related to grape variety. This would require a large number of different wines within each variety and still it would be a difficult task since the production methods and terroir may greatly affect the flavour of the wine. Furthermore the study concludes that the reduction method is important to the perceived flavour and volatile profile. The flavour of reduced stocks with wine was observed to generally depend on the reduction method and moreover the suggested precipitation of phenolics (when heated with meat proteins) may decrease the astringency of high-tannic red wines.

13 DISCUSSION OF MEAT STOCK REDUCTION

Preparation of a stock is a relatively simple kitchen process involving cooking of the ingredients in water which may be followed by boiling the stock down. Despite the apparent ease of the process, there are some challenges related to achieving the ideal stock for a particular purpose which meets the demands for flavour, viscosity and clarity. Thus a large number of prescriptions are associated with stock preparation, as explained in more detail by This (2009d). Understanding the process from a scientific point of view and not least elucidating the rationale behind the prescriptions is not straightforward. As also demonstrated by This (2009d), a large number of questions related to the optimal choice of ingredients and preparation method can be raised. These questions are of interest to home cooks, restaurant chefs and the food industry.

Scientists have studied meat flavour formation intensively but only few studies have looked into the details concerning stock preparation. Knowledge generated by scientists on meat flavour in general as well as branches of physical chemistry and sensory science can be applied to understand and predict the important mechanisms behind stock preparations as has been done in this thesis. Nevertheless, in order to understand changes in flavour, texture and appearance upon cooking and reduction of a stock and how this may be controlled, more studies must be conducted on this particular topic. Preparation of a successful stock, as with many other dishes, still mostly relies on the experience of the chef and prescriptions handed down. A better scientific understanding of the basic steps in stock preparation will support the chef in making the right choices and controlling the process as well as the food industry in producing the best possible convenience products to those that do not prioritise the time consuming stock production themselves.

Elucidating the mechanisms behind stock reduction is an important step towards more precise directions on how to prepare the stock, controlling the flavour of the outcome. A first step toward understanding the last part of the stock preparation process, the reduction, is taken by the experimental study published in Paper III. The results have given an increased insight into the possible chemical reactions and the physical changes that occur during reduction of meat stock, affecting perceived flavour and the volatile compounds. The study has provided new knowledge about how flavour changes with time as well as the effect of changing the power input and accordingly the rate of reduction. An important outcome of the study is that the decrease in volume upon reduction, as often referred to by cooks (and also expressed as the concentration factor) may determine the texture and the concentration of taste compounds but this alone does not predict the flavour. The advice based on these results is to understand the effect of the reduction time and to control the reduction time relative to the concentration factor. The rationale behind this is that the time by itself determines some drastic changes in concentration of volatile compounds with time. This is explained by the combined effect of evaporation of compounds as well as breakdown and formation of compounds due to chemical reactions such as Maillard reactions.

Although the study resulted in some actual advice about controlling the relation of concentration factor and reduction time, there are still many questions to be answered regarding meat stock preparation, even if just focusing on the reduction process alone. One particular issue is the role of oil in the stock. This problem is raised by This (2007e) and also by Ubbink (2010). Does the small amount of oil present in the stock during cooking and reduction retain important aroma molecules upon cooking, and in case so will these be released and thus be available for perception when eating? Or does the oil present generate undesired lipid oxidation

products? Accordingly, is there an advantage of having a certain amount of oil in the stock upon reduction or should everything ideally be removed before reduction in order to obtain the best flavour? These are some obvious questions for further investigation.

Another noticeable outcome of the study on stock reduction was that the longer the stock was reduced the less one stock could be distinguished from another. Since a large number of the initial volatile compounds were lost and new ones formed, the two initially rather different stocks became more similar with regard to volatile profile and sensory characteristics. The same was seen in the study on beef stock with red wine (paper IV). When reducing the two different wines, the initial aroma was to a large extent lost and they became more similar. Thus the flavour outcome of a stock or wine reduction depends less on the initial volatile composition and more on the flavour generation upon the heating process. In other words, when choosing a wine for cooking, the fine aromas of many red wines are not important but the non-volatile components (sugar, acids, tannins) may on the other hand be very important to the flavour after cooking since they will be concentrated and serve as precursors to the generation of new flavours. In the study it was also seen how reduction of wine and stock separately resulted in a clearly different flavour than when combining them before reduction. This is explained by the complex flavour generation during reduction and the corresponding dependence on the precursors available.

The study on stock reduction with wine also raised an issue of mouthfeel in the stock reduction in the wine. In the sensory analysis of the stocks with red wine, the particulate mouthfeel descriptor was important in distinguishing the stock samples. Based on a hypothesis generated from cookbooks and scientific literature, the particulate mouthfeel observed was explained as precipitation of tannins from red wine with meat proteins in the stock. It was shown that the more astringent and bitter wine, the Cabernet Sauvignon, gave rise to higher ratings of particulate mouthfeel. The precipitation is suggested to occur when reducing wine and stock together. In this study the precipitate may have been formed in upon reducing of wine and stock together but the precipitate has in such case been removed by filtering before sensory analysis. The stock samples prepared by reducing wine and stock separately and then mixing were on the other hand perceived to have a particulate mouthfeel. This is argued to be the result of tannin-protein precipitation upon reheating of the mixed stock and wine sample prior to sensory evaluation. This supports that 30 min of cooking the wine and stock together, as suggested by Peterson (2008), is enough to obtain the desired precipitation which may reduce the bitterness and astringency from the wine tannins.

Having understood the reduction process a little better, it is possible to think of new ways of reducing a stock. The traditional stock reduction can be seen roughly as three processes with great effect on flavour, that happen simultaneously: 1) concentration of non-volatile compounds due to decrease in volume upon evaporation of water, 2) loss of volatile aroma compounds to the surrounding air and 3) heat-induced chemical reactions leading to break-down of some compounds and generation of others. It is interesting and not difficult to imagine that new ways of preparing a stock reduction or wine reduction could be developed as an alternative to the traditional boiling down of the stock or wine. Assuming that the loss of volatile compounds, as observed upon boiling a stock or wine down, is generally not desired, the possible new course of action should imply concentration of existing non-volatile and volatile compounds and formation of new.

The concentration of compounds by eliminating water is one step that could easily be achieved in other ways than by boiling the stock. Freeze-drying is one high-technology way to eliminate water without applying

heat. Another possible way would be to freeze-concentrate it. Freeze-concentration involves crystallization of the water by freezing and then separating the pure ice crystals from the concentrated stock. This is a technique which Heston Blumenthal from The Fat Duck has applied to reduction of stocks, apparently with great success. Heston describes this technique for stock reduction in his cookbook, *The big Fat Duck cookbook*. The resulting concentrated stock is described to be very clear and having ‘more of the really fragrant top notes’ (Blumenthal 2008b).

Removal of water alone without applying heat would without doubt give a completely different result. The initial flavour would simply be concentrated and the loss of volatile compounds would be avoided. The flavours formed by heating in a traditional stock would on the other hand be missing. Such compounds may however be added separately and in this way the ideal flavour characteristic may be achieved.

Another possible alternative to avoid loss of aroma compounds during wine or stock reduction is to trap the evaporated aroma compounds and transfer them back to the wine or stock. This technique is used in other branches of the food industry as for example in the production of juice where it is desired to recover the aroma compounds upon heating (conservation) of the product (Kollmannsberger and Berger 1994). The process involves fractional distillation, a separation based on differences in volatility of the different constituents of a mixture. The idea in this context involves boiling off the volatile aroma compounds present initially in the stock or wine, trapping these compounds, and then transferring the desired aroma fractions back to the wine or stock when the final concentration factor has been reached.

The idea of reducing a stock by other means than boiling has also been discussed and explored by Ubbink (2010) who has experimented with freeze-drying of stocks as an alternative method to traditional reduction. He reports that the result of freeze drying stock is a concentrated stock similar in texture and mouthfeel to a traditional stock reduction but very different in flavour. The flavour of the stock prepared by freeze-drying has as expected much more of the flavour associated with the original ingredients. Ubbink (2010) has further optimized the freeze-dried stock by briefly heating it in order to induce some of the flavour generating reactions. In this way the concentration of non-volatile compounds and the generation of new compounds have been separated as two individual steps in preparation of stock reductions.

The potential in optimizing the stock reduction is large. The flavour, texture and clarity in a traditional stock reduction can be optimized by a greater insight into the mechanisms behind the changes happening upon the traditional evaporation process. An increased understanding of the process by the chef will open up new possibilities to control it and to get the desired result for any purpose: an ambition for the enthusiastic chef whether working in the traditional or experimental kitchen. The mastery of new techniques like freeze-drying enhances the chef to be even more creative. Optimizing and control of the stock reduction has likewise great potential in the food industry.

14 CONCLUSION

Molecular Gastronomy is a scientific approach to gastronomy and is considered a sub-field of food science at several Universities across the world. As opposed to traditional food science, MG focuses on small scale production and obtaining the ultimate meal experience. The purpose of Molecular Gastronomy is to 1) optimize the sensory quality of ingredients in the primary production, 2) obtain a scientific understanding of ordinary and innovative kitchen preparation and 3) obtain a greater insight into the perception of a meal. A greater understanding of what makes a meal good has great potential to improve the quality of meals in the future. This may include high quality healthy meals in food service, development of magnificent meal experiences in restaurants and also an increased knowledge of meal preparation by the home cook. Furthermore Molecular Gastronomy has great potential to be used for teaching basic scientific principles to students. In general a scientific approach to food and cooking serves as an excellent way of communicating science to the public. There are however large challenges connected to working in this field between science and gastronomy as for example establishing a fruitful collaboration between scientists and chefs. Furthermore the challenges include how to obtain funding for the work and how to communicate the aims and potential benefits of Molecular Gastronomy to the society.

The scientific exploration of meat stocks, in part two of the thesis, identifies some important aspects of flavour development upon stock preparation. The results obtained from the two scientific investigations of meat stock reduction suggest ways of optimizing the process and controlling the flavour development. Based on the results obtained in Paper III, chefs are advised to understand the effect on flavour of reduction time versus concentration factor (the degree of reduction with respect to volume). Results from paper III illustrate how flavour develops upon reduction due to evaporation of aroma compounds and the simultaneous formation of new compounds due to heat induced chemical reactions, such as Maillard/Strecker reactions. The results from paper IV suggest that the flavour characteristics of a wine are important to the flavour after cooking although aroma compounds are quickly expelled upon cooking. Thus a wine for cooking should be chosen mostly based on its content of non-volatile taste compounds, whereas the fine aroma of wines is lost. The results from Paper IV further illustrate how flavour development during preparation of reduced stocks with red wine depends on the preparation method (reducing wine and stock together versus separately). Based on a hypothesis derived from cookbooks and scientific literature the particulate mouthfeel perceived by the sensory panellists is explained by precipitation of wine polyphenols (tannins) and meat proteins in the meat stock with red wine. Although more studies are needed to confirm this, the results suggest that wine polyphenols interact with proteins from the meat upon heating and this leads to a decline in the astringent polyphenolic compounds in the meat stock with red wine.

In general, the outcomes of the investigations on meat stock reduction do not give rise to specific prescriptions to chefs but only to guidelines explaining some mechanisms behind the preparation technique which can be used as a tool for the chef to advance in stock preparation. The results further serve to elucidate common cookbook prescriptions on these matters.

Through the work of the present PhD thesis, progress has been made in establishing Molecular Gastronomy as a scientific sub-field of food science by presenting relevant topics and discussing the aims and relevance for society. Furthermore progress has been made in elucidating the important mechanisms behind stock

preparation, in particular stock reduction. There are however still many open questions concerning meat stock preparation, as described in part two of the thesis. Meat stock preparation is one out of a countless number of kitchen preparations which have not previously been investigated scientifically, but particularly due to the long tradition and significance of stocks in our food culture meat stocks deserve considerable attention. Thus further studies on meat stock preparation as well as other studies in the field of Molecular Gastronomy are encouraged.

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