Understanding the reactivity of formulated products to optimize quality and safety: the case of newly formed volatile compounds.

Barbara Rega

Université de Bourgogne

Habilitation à Diriger les Recherches

Understanding the reactivity of formulated products to optimize quality and safety: the case of newly formed volatile compounds

Présentée par Barbara Rega

A Paris le 11 juin 2020 devant le jury :

Erwan Engel Directeur de recherche INRAE (Unité QuaPa)	Rapporteur
Isabelle Souchon Directrice de recherche INRAE (Unité SQPOV)	Rapporteur
Fréderic Tessier Professeur d'Université Université de Lille	Rapporteur
Gaëlle Arvisenet Professeure d'Université Université de Bourgogne	Examinatrice
Elisabeth Guichard Directrice de recherche INRAE (Unité CSGA)	Examinatrice
Paola Vitaglione Professeure associée, HDR Università Federico II di Napoli	Examinatrice

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Acknowledgment

First of all, I would like to thank all the colleagues, teachers and researchers who worked with me, and gave me the pleasure of collaborative work.

I thank Elisabeth Guichard who was my mentor during the PhD thesis years and long after, Gérard and Elisabeth Cuvelier who were life and work examples. Francesco Addeo and Tonino Malorni who gave me the greatest confidence to launch me into a career outside Italy, as well as Hubert Richard, who enchanted me with his enthusiastic desire to transfer knowledge.

A big thank to Pierre Giampaoli who took me under his wing when I started in the laboratory of chemistry of natural substances. He's the one with the bright idea of online monitoring of cooking compounds.

Thank from the bottom of my heart to Catherine Bonazzi who has always supported me and with whom I have great pleasure to collaborate. Similarly, my most sincere thanks go to Véronique Bosc, Valérie Camel, Marie-Noëlle Maillard, Camille Michon and Catherine Beal, colleagues with unwavering support, wise advice and remarkable vision.

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I don't forget Marwen Moussa, Isabelle Laissy, all my FIPDes colleagues and students with whom I share so many inspiring educational, international and human adventures.

Finally, I would like to thank the jury for agreeing to evaluate this work: Gaëlle Arvisenet, Erwan Engel, Elisabeth Guichard, Isabelle Souchon, Fréderic Tessier and Paola Vitaglione… ..In these strange times of Covid-19 ……

Foreword

My mission as a teacher-researcher is that of acting at the heart of the knowledge triangle. I am committed 1) by training the decision-makers of tomorrow on an international scale, 2) by promoting innovative cooperative projects and 3) by bringing my contribution to knowledge for a rational and sustainable production of food, within my French and international scientific network. My contributions fully participate in the first strategic axis of the SPAB Department of AgroParisTech: "Reasonable construction of sustainable food and bioproducts" with in particular the understanding of the link between formulation and reactivity for the construction of food properties. Within the UMR 1145 Genial, which has become UMR Say Food since January 2020, I am interested in understanding the influence of formulation and process parameters on the generation and degradation of newly formed compounds which have sensory and health interest, in the perspective of reasoning the design of food. My research feed my teaching activities, in particular about building the quality and safety of food products and, more generally, about the innovation of sustainable food systems.

Organization of the manuscript

This manuscript is organized into several chapters. I have tried to include a reasonable number of figures, diagrams, tables and appendices in order to make it easier to read. **Chapter 1** contains my detailed curriculum with an overview of my research and teaching activities as well as collective responsibilities. In **Chapter 2**, I present a summary of my research activities. Here I have chosen to exclusively present research around reactivity and newly formed compounds. **Chapter 2** is then organized **into three axes** bringing together three main areas of investigation: (I) the development of analytical methodologies; (II) The study of the links between process, formulation and quality determinants; (III) the understanding of reaction mechanisms and kinetics. **Chapter 3** presents a summary of my teaching activities and links with research. **Chapter 4** is dedicated to giving you an overview of research management activities until March 2020. **Chapter 5** presents the perspectives that I envisage in the short and medium terms and the **chapter 6** presents an exhaustive list of my scientific production. **Annexes** are proposed in limited number. The first contains a selection of personal articles related to Chapter 2, the others present interesting elements of detail compared to what is presented in the previous chapters.

Abreviations list

1-D : 1-Déoxyosone

2,5 : 2,5-Diméthylpyrazine

2,6 : 2,6-Diméthylpyrazine

3,4-D : 3,4-Didéoxyosone

3-D : 3-Déoxyosone

3-MB : 3-Méthylbutanal

AGE : Advanced Glycation End-products, produits avancés de glycation

APT : AgroParisTech

AS : Absorbance spécifique

C : Caramélisation

CAD : Charged Aerosol Detector

CIRC : Centre International de Recherche sur le Cancer

CM : Cours magistral

CML : N-ε-Carboxymethyllysine

CMR : Composé cancérigène mutagène reprotoxique

CNF : Composé néoformé

CNFI : Composé néoformé indésirable

CNFV : Composé néoformé volatil

CSGA : Centre des Sciences du Goût et de l'Alimentation

DAD: Diode Array Detector

DDMP : 2,3-Dihydro-3,5-dihydroxy-6-méthyl-pyranone

DIT : Dublin Institute of Technology

DS : Dégradation de Strecker

EI : Etalon Interne, Internal standard

EMJMD : Erasmus Mundus Joint Master Degree

ENSIA: Ecole Nationale Supérieure des Industries Agroalimentaires

F : Fructose

FL : N-ε-Fructosyllysine

G : Glucose

GC/MS : Chromatographie en phase gazeuse couplée à la spectrométrie de masse

GC-O : Chromatographie en phase gazeuse couplée à l'olfactométrie

GC-O-D : Chromatographie en phase gazeuse couplée à l'olfactométrie directe

GCxGC/ToF-MS : Chromatographie en phase gazeuse bidimensionnelle couplée à la spectrométrie de masse avec analyseur à temps de vol

GéPro : Génie des produits

HMF et 5-HMF: 5-Hydroxymethylfurfural

HS trap : Extraction headspace avec piégeage

HS-GC/MS : Extraction headspace couplé à la chromatographie en phase gazeuse avec détecteur de masse

IMARS : International Maillard Reaction Society

L : Leucine

LO : Lipid Oxydation

MC: Maître de conference

MP : 2-Méthylpyrazine

MR : Maillard reaction

OL : Oxydation lipidique

P : Pyrazine

PPB : Partie par milliard (10^{-9})

PPM : Partie par million (10^{-6})

PRM : Produit de la Réaction de Maillard

PUFA : Polyunsaturated Fatty Acids (Acides Gras Polyinsaturées)

RSM : Response Surface Modeling

S : Saccharose

SPME : Solid Phase Micro Extraction (micro-extraction en phase solide)

TD : Thermo-désorption (chapitres 2 et 5) ; Travaux Dirigés (chapitres 1 et 3)

TP : Travaux pratiques

TUDublin : Technical University Dublin (anciennement DIT)

UHPLC/MS-Tof: Ultra High Performance Chromatography / Mass Spectrometry / Time of Flight (chromatographie liquide à ultra haute performance couplée à la spectrométrie de masse avec analyseur à temps de vol).

UMR 0782 SayFood : Unité Mixte de Recherche Paris-Saclay Food and Bio-product Engineering

UMR 1145 Genial: Unité Mixte de Recherche Ingénierie Procédés Aliments

UMR SCALE : Unité Mixte de Recherche en SCience de l'Aliment et de l'Emballage

UMRA : l'Unité Mixte de Recherche sur les Arômes

UNINA : Università degli Studi di Napoli Federico II

WUR : Wageningen University and Research

Glossary

Newly formed compound: Chemical substance formed during the process of technological transformation and/or industrial or household culinary preparations of foodstuffs by chemical reactions. Exposure of the consumer to certain newly formed substances through food may possibly be associated with undesirable effects which may appear in the more or less long term. Certain newly formed compounds are therefore defined as undesirable (https://www.anses.fr/fr/system/files/GBPH2014SA0036.pdf).

Réseau CANAL-ARLE : «Flavor-food-packaging interactions, stability during storage, release and perception of flavors during mastication», réseau RARE, Ministère de la Recherche.

Projet ANR–Reactial: « Prediction and control of the appearance or disappearance of reaction markers during food processing and preservation». Programme National de Recherche en Alimentation et nutrition humaine ANR-06-PNRA-023.

Projet ANR–ALIA DOMINOVE: « Influence of domestic heating on the sensory and nutritional characteristics of pre-fried industrial products».

Projet ANR SATIN: « Identification of the consequences of the aging of the non-stick coatings of baking molds on the chemical and physico-chemical characteristics of cereal products such as sandwich loaves».

Projet DIM-ASTREA : « What evolution of production systems, organizations and products to develop sustainability and competitiveness of the food sector? ».

Projet ITN FOODENGINE: "Enginomics in food quality design: the case of shelf-stable fruit-, vegetable and legume-based foods». Programme ITN Call-H2020-MSCA-ITN.

Chapitre 1
Curriculum Vitae

Chapitre 1 : Curriculum Vitae

État civil et situation professionnelle

Barbara Rega
Née le 22 avril 1973 à Naples (Italie), Nationalité italienne; Mariée – 1 enfant (2008)

Maître de Conférences titulaire
(7ème échelon), section CNECA n° 4 (chimie, technologie, science des aliments)

Etablissement:
AgroParisTech (APT) - département de Science et Procedés des Aliments et Bioproduits (SPAB)
UMR 0782 SayFood Paris Saclay Food and Bioproducts Engineering, AgroParisTech- INRAE
1 avenue des Olympiades 91744 MASSY
☎ : 01.69.93.51.33, *e-mail* : barbara.rega@agroparistech.fr

Titres et diplômes

2003 **Doctorat** en **Science des Aliments**, mention TB avec félicitations du jury. Cotutelle entre l'Université de Bourgogne et l'Università di Napoli « Federico II ». Thèse soutenue le 2 décembre 2003, devant le jury présidé par le professeur L. Moio (rapporteur) et composé des professeurs A. Razungles (rapporteur), M. Di Matteo (examinateur), L. Chianese (co-Directeur) et du Dr. E. Guichard (Directeur).

2000 **Habilitation à l'enseignement secondaire** (équivalent CAPES) en Chimie Agro-alimentaire délivrée par le Ministère de l'Education Nationale Italien.

1998 **Habilitation à la profession de chimiste** obtenue le 22 mai 1998 en Italie.

1998 **Diplôme Universitaire en Chimie** ("Laurea in Chimica": EQF niveau 7), **option biochimie**, Università di Napoli « Federico II » (note 105/110).

1992 **Baccalauréat type série L** (Italie).

Formations et stages complémentaires

Encadrement de la recherche :

Ecole des doctorants et encadrants « EDEN » (2019, INRA, 5 jours) ; Techniques d'animation collective (2017, INRA, 2 jours) ; Travailler dans un contexte multiculturel (2016, Formation Permanente AgroParisTech, 3 jours).

Management :

Management de proximité (2018, INRA, 5 jours) ; Management d'équipe (2015, Formation Permanente AgroParisTech, 3 jours) ; Gestion du temps et management (2013, Formation Permanente INRA Jouy en Josas ; 6 jours) ; Gestion de conflits (2011, Formation Permanente AgroParisTech, 1 jour) ; Conduite de projet (2011, Formation Permanente INRA Jouy en Josas ; 4 jours).

Communication :

Formation en anglais scientifique et en « Managing meeting » pour les Chercheurs de l'école doctorale ABIES (2009-2011, formation hebdomadaire) ; Perfectionnement en conversation anglaise (2003, formation doctorale, Université de Bourgogne, 15 sessions) ; Enrichir sa communication (2003, formation doctorale, Université de Bourgogne, 3 jours) ; Communication interpersonnelle et management (2003, formation doctorale, Université de Bourgogne, 3 jours).

Pédagogie :

Formation Pédagogique pour Enseignants Chercheurs (2004-2005, Ministère de l'Agriculture, de l'Alimentation, de la Pêche et des Affaires Rurales, 7 jours) ; Mise en place de grilles tutorées (2019, Ministère de l'Agriculture, de l'Alimentation, de la Pêche et des Affaires Rurales, 1 jour).

Développement professionnel:

Bilan des potentiels et développement du projet professionnel personnel (2002, formation permanente INRA Dijon, 5 jours) ; Doctoriales de l'Université de Bourgogne. Messigny et Vantoux, (2003, formation doctorale, Université de Bourgogne, 6 jours) ; Analyse statistique mono-variée et multi-variée (2002 et 2003, formation permanente INRA Dijon, 9 jours) ; Introduction au monde de l'entreprise (2000, formation professionnelle, Ministero dell'Università e della Ricerca Scientifica e Tecnologica/Tecnogen, Caserta - Italie, 10 sessions).

Cursus professionnel, fonctions exercées, mobilité

Depuis 2005 **MC titulaire en chimie de l'aliment** à l'ENSIA (Jusqu'à 2008) et AgroParisTech (dès 2009). Rattachement à l'UMR SCALE (de 2004 à 2009) ensuite UMR Genial dès 2009.

2004 - 2005 **MC stagiaire** en chimie de l'aliment à l'ENSIA.

2001 - 2003 **Doctorante** à l'Unité Mixte de Recherche sur les Arômes INRA-ENESAD (UMRA), Dijon, sous la direction du Dr. E. Guichard. Financement ministériel italien. *Texture-Flavour interactions: How physical-chemical data explain sensory perception in orange juice.*

2000 - 2001 **Allocataire de recherche pré-doc** à l'UMRA, sous la direction du Dr. E. Guichard. Financement ministériel italien.

1998 - 2000 **Assistante de recherche contractuelle (eq. IE)** — Laboratoire de biochimie, Istituto di Scienze dell'Alimentazione, Centro Nazionale delle Ricerche (*ISA-CNR*) — Avellino, Italie. *Development of modern mass spectrometric methods for the structural characterization of milk and cereal proteins.*

Domaines de compétence

- Qualité et sécurité des produits agro-alimentaires
- Réactivité chimique et réaction de Maillard
- Arômes alimentaires
- Chimie analytique
- Composés néoformés

Responsabilités, fonctions et appartenance à des commissions au service de l'établissement

Responsable de l'équipe de recherche Calipro de l'UMR Genial (25 permanents), de 2017 à 2019.

Coordinatrice de l'Erasmus Mundus Joint Master Degree in Food Innovation and Product Design (EMJMD FIPDes, www.fipdes.eu), de 2010 à présent.

- Présidente du Comité de Consortium des Universités partenaires (Lund University –SE–, Dublin Institute of Technology –IE– Università Federico II di Napoli –IT – AgroParisTech/Université Paris-Saclay –FR)
- Coordinatrice pédagogique et stratégique
- Animatrice de l'*International Advisory Board* (Alumni, membres scientifiques extérieurs, membres industriels, Partenaires Associés)
- Présidente du comité de sélection et recrutement

Membre du comité de pilotage du Master Spécialisé IPCI (Ingénierie de Produits à l'Interface Cuisine-Industrie, dès 2013).

Membre du comité de perfectionnement de la mention de master Nutrition Santé Aliment (NSA) de l'Université Paris Saclay (dès 2016)

Membre élu du Conseil d'unité de l'UMR 1145 (2017- 2020)

Membre du comité scientifique de la chaire I3F (chaire Industrielle d'Ingénierie et Innovation Frugale), de l'Université Paris Saclay (2015-2019).

Activités d'expertise

- Montage et management de **programmes européens de formation** (Eurodoc'Agro de 2012 à 2016; EM-IDEA, EM-ACE, EACEA Coordinators' clusters, ProDeJIP).
- Appartenance à des **comités de lecture de revues scientifiques internationales** (Food Chemistry, Flavour and Fragrance Journal, Journal of Food Engineering, Journal of Agricultural and Food Chemistry, 3-6/an).
- Expertise en **chimie de l'aliment, arômes et formulation** dans le cadre de projets R&D industriels: Grand Marnier (2009-2011), Ynsect (2012), Danone Research (2013), Yoplait (2016), Nestlé (2019).

Appartenance à des sociétés savantes nationales et internationales

- Membre fondateur du réseau international ProDeJip (*International association for the PROmotion and DEvelopment of Joint International Programmes in higher education*)
- Membre d'IMARS (International Maillard Reaction Society)
- Membre de la SCF (Société Chimique de France)
- Membre de l'AIC (Académie Italienne de Cuisine)

Activités de communication scientifique

Organisatrice du séminaire scientifique international « FIPDes Day »

1 séminaire/an, 150 participants, env. 25 pays, 5 sessions plénières, 2 sessions posters, 5 stands de *Job-dating* international, 3 prix de communication scientifique. Valorisation par 1 livret d'actes de colloque/an, 1 newsletter, articles web dans les canaux institutionnels des 4 universités partenaires de FIPDes (http://www.fipdes.eu/?FIPDes-Day-122).

Conférencière invitée

Dans le cadre d'évènements et séminaires liés à la recherche (Club Ecrin 2003; Action Cost 926 2006; Rencontre AgroParisTech de l'Alimentation, 2013; Ecole doctorale ABIES - *Symposium Doc'd'Avenir*, 2016 ; Séminaire National FMARS, 2018.)

Dans le cadre d'évènements liés à l'enseignement et au rayonnement international de l'enseignement supérieur (RUE-Rencontres Universités Entreprises, Paris, 2012; Agence Européenne EACEA, Bruxelles 2017; Ambassade de France en Irlande – *Réseau FICHAT*, Dublin 2018 ; 14ème rencontres F. Rabelais, Tours, 8 décembre 2018).

Activités de vulgarisation scientifique (*Conférences/Ateliers/Emissions)*

- JT France 3 Bourgogne, participation au tournage d'un dossier sur la recherche sur les arômes, 2001.
- Journées portes ouvertes Ensia/ Conseil de l'Essonne : conférence grand public sur *« Les arômes alimentaires»*, Massy, 2005 et 2006.
- Radio Campus, Dijon : invitée de l'émission « Le microscope et la blouse» sur *« les sciences de l'alimentation»,* sept. 2005. *http://experimentarium.u-bourgogne.fr/pageshtm/presse/microblou2/MB_BarbaraR.html*
- La nuit des chercheurs, atelier grand public sur « *la réaction de Maillard et les arômes»*, Université de Bourgogne-Dijon, 2006.
- Incontro regionale annuale dell'Accademia Italiana di Cucina, conference invitée sur «*I profumi della tavola: Gli aromi in cucina, liaisons dangereuses tra scienza e gastronomia»*, Avellino, Italie 2009.
- Emission E=M6 sur *Chocolat, pâtisserie: les secrets scientifiques de nos desserts*, diffusée le 24 novembre 2013.
- Salon International de l'Agriculture : édition, développement et animation d'un jeu interactif et quiz en anglais sur l'innovation alimentaire, conférence grand public sur « L'innovation sans frontières », Stand AgroParisTech, Paris, février 2015.
- Site internet INRA : Article de divulgation scientifique : « Cuisson des gâteaux et réactions chimiques » (publié le 22/11/2017), http://www.inra.fr/Grand-public/Alimentation-et-sante/Toutes-les-actualites/Cuisson-des-gateaux-et-reactions-chimiques
- Conférence *« Gluten Arômes et Fantaisie, digressions autour du babà* », tenue à l'Accademia della Cucina Italiana dans le cadre du Symposium « Cucina italiana – Cuisine française Influences réciproques

au cours des siècles », Ambassade d'Italie, Paris, 19 mai 2019.
http://italieendirect.italieaparis.net/article/cuisines-italienne-et-francaise-%3A-influences-reciproques-339/.

Participation à des réseaux de recherche nationaux et internationaux

Club ECRIN (2001-2006) : Club Arômes alimentaires d'ECRIN. Présentations, participation aux groupes de travail.

Réseau transversal INRA ITF (2003-2005): « Interactions texture-flaveur ». Approche multi-échelle à la compréhension des mécanismes et des processus responsables de l'élaboration de la qualité et de la perception des aliments.

COST Action 927 (2005-2010): « Thermally processed foods, possible health implications». Work group 1: analytical methodologies. Impact des technologies, approches analytiques et exposition au risque des composés néoformés.

IMaRS (2006-) : International Maillard Reaction Society.

FMaRS (2016-) : Comité d'experts francophones sur la glycation et la réaction de Maillard.

Participation à des projets de recherche et réseaux nationaux et internationaux

CANAL-ARLE (2002-2005)**:** «Interactions arômes-aliments-emballages, stabilité en cours de conservation, libération et perception des arômes en cours de mastication », 14 Partenaires industriels et 9 Partenaires publics. Financeur : Ministère de la Recherche (réseau RARE) + Industriels. Participation au WP4.

Projet ANR–Reactial (2007–2010): « Prédiction et contrôle de l'apparition ou de la disparition de marqueurs réactionnels au cours de la transformation et de la conservation des aliments». Participation aux WP2, WP3 et WP4. Responsable scientifique pour l'UMR SCALE. Encadrement thèse S. Fehaili.

Projet ANR–ALIA DOMINOVE (2010-2013) : « Influence du réchauffage domestique sur les caractéristiques sensorielles et nutritionnelles des produits industriels pré-frits ». Participation aux WP2.

Projet ANR SATIN (2012-2015) : « Identification des conséquences du vieillissement des revêtements antiadhésifs des moules de cuisson sur les caractéristiques chimiques et physico-chimiques de produits céréaliers type pains de mie ». Collaboration thèse L. Huault.

Projet DIM-ASTREA (2013-2016) : « Quelle évolution des systèmes de production, des organisations et des produits pour développer durabilité et compétitivité du secteur de l'alimentation ? ». Co-encadrement thèse J. Bousquières.

Programme ITN Call-H2020-MSCA-ITN- 2017 (2018-2022): «FOODENGINE: Enginomics in food quality design: the case of shelf-stable fruit-, vegetable and legume-based foods». Trois partenaires publiques et 6 partenaires privés. Direction de la thèse de S. Krause.

Participation à des jurys (membre ou rapporteur)

- **Jurys de MCF** : Chimie analytique et santé (2014, AgroParisTech, suppléant), Ecotoxicologie (2015, AgroParisTech, suppléant), Neurosciences sensorielles (2016, Université de Tours, examinateur).
- **Jurys de thèse :** Pauline Poinot (Oniris, Nantes, 2009), Yacine Merabtine (Université de Bourgogne, 2010), Riad Mabazaa (AgroParisTech, 2010), Souad Fehaili (AgroParisTech, 2010), Sophie Deterre (AgroParisTech, 2012), Cynthia Helou (UniLaSalle-Beauvais, 2014), Emilie Korbel (CIRAD, Montpellier, 2014); Josselin Bousquières (AgroParisTech, 2017), Mayela Cepeda Vazquez (AgroParisTech, 2017), Jeehyun Lee (AgroParisTech 2019).
- **Présidente du jury international de sélection** du master EMJMD FIPDes depuis 2011. M1 : Environs 400 candidats par an en M1 : 25 étudiants.
- **Membre des jurys de fin d'études** du cursus master et ingénieur AgroParisTech en tant que rapporteur ou examinateur (environ 10/an).

Participation à des comités de thèse

Lamia ait Ameur (2006), Sophie Cheriot (2006), Gregory Loarec (2014), Juliette Palier (2021).

Activités d'enseignement

Domaine de la chimie alimentaire, sécurité sanitaire des aliments, analyse chimique et ingénierie de l'innovation. Des nombreux enseignements en coordination et participation dans le cursus ingénieur d'AgroParisTech et master de l'Université Paris Saclay – BAASE (Biodiversité, Agriculture et Alimentation, Société, Environnement). Création, responsabilité de modules, enseignement et coordination de formation. **208 heures équivalentes TD** en moyenne sur les dernières 5 années.

Contribution au Cursus Ingénieur

Contribution à 3 Unités d'Enseignement dans le domaine de la sécurité des aliments, la biochimie et les arômes alimentaires (CM, TD, TP):

- Additifs et arômes alimentaires (2ème Année)
- Food safety and risk analysis throughout the food chain (2ème Année)
- Arômes alimentaires : formulation et mise en œuvre (3ème Année))

Contribution à l'enseignement de 3ème cycle

Mention NSA, Parcours international Food Innovation and Product Design Erasmus Mundus Joint Master Degree (FIPDes)

- Montage et coordination générale (2009-)
- Coordination pédagogique M1 et M2 (120 ECTS)
- Activités d'enseignement en anglais (CM, TD, TP, encadrement de projets, tutorat) dans le cadre des 6 Unités d'Enseignement: Compréhensive Food Science & Analysis ; R&D Junior Project ; Reaction Engineering applied to food matrices ; Senior project in Food Design and Engineering; Food Safety through the supply chain, MSc. Thesis, FIPDes Introduction Module. Constituant la majorité de la charge statutaire à présent.

Mention NSA, Parcours Ingénierie des Produits et des Procédés (IPP)

- Activités d'enseignement (CM, TP, encadrement de projets, tutorat) dans le cadre de l'UE Génie de la réaction appliqué aux matrices alimentaires.

Mention NSA, Parcours Analyse des Risques Sanitaires liés à l'Alimentation (ARSA)

- Cours magistral sur les composés néoformés dans le cadre de l'UE « Qualité et sécurité chimique des aliments et des bioproduits » (2005-).

Cursus Post-*Master AgroParisTech Executive* : *Master IPCI* « Ingénierie des produits à l'interface Cuisine-Industrie »

- Activités d'enseignement (CM, TP, encadrement de projets, tutorat) sur les « arômes alimentaires » dans le cadre de l'UE « Outils de formulation » (2010 -).

Chapter 2
Overview of the research activities

Chapter 2: Overview of the research activities

Introduction

Scientific context

The societal expectations of naturalness and sustainability of our communities converge on the opportunities for valorization and responsible use of plant resources (e.g. new protein sources), to make them foods that meet, on one side, the current health needs (e.g. nutrition, food safety) and, on the other side, the expectations of practicality, taste and ethics (e.g. local eating and globalized world).

The emergence of the concept of **sustainable food systems** shows that a "holistic" reflection on the entire food chain / circle is being put in place with the aim of taking into account environmental and health issues together with economic issues. Sustainable processing chains must, for example, make it possible to conserve / exploit the properties of raw materials as much as possible or to reinforce their potential through formulation and process for uses at different possible levels.

By meeting these global trends, food innovation explores the use of new ingredients and processes, with the need to minimize the use of certain additives or components and, at the same time, meet the multiple binding criteria of the quality. **However, as soon as these are products subjected to heat treatments (e.g. cooking), the question must be asked of how these changes in formula / process could impact the reactivity of these foods.** In fact, the main thermal reactions can lead to the formation of newly formed compounds which are desirable in certain cases (e.g. flavor compounds), undesirable in other cases (potentially toxic compounds, off-odors). The dynamics in the risk assessment for newly formed compounds over the recent years (e.g. acrylamide[1]) shows us that it is important to study product & process interactions in order to understand, control and predict the risk/benefit balance related to newly formed compounds and thus ensuring the overall quality of processed products.

Structural framework and organizational context of my research work

My research aims to participate in this dynamic, which is also at the heart of the strategic project of the **SPAB[2] Department of AgroParisTech**, as well as in one of the challenges of the **CEPIA department of INRA,** which became INRAE TRANSFORM department on January 1, 2020. My research activities were part of the first thematic field of the CEPIA department ("Characterizing and modeling the structures of raw and processed materials up to finished products") aimed, more precisely, at the challenge "reasoned conception of the quality of food and bioproducts", at the interface of two of the seven programmed actions: (1) Characterize the raw materials at different scales and at the different stages of transformation and (2) Develop tools to reason the quality according to a multi performance logic.

Since my integration into ENSIA then AgroParisTech, I have been successively attached to four structures:

2004 to 2008: The Joint Research Unit on Sciences of Food and Packaging (UMR SCALE 1211, ENSIA-CNAM-INRA) resulting from the merger between the CSNaac Laboratory of ENSIA, the Chair of Industrial and Agrifood Biochemistry CNAM and an INRA Laboratory in Jouy-en-Josas specialized in the field of packaging.

2009 to 2019: The Joint Research Unit on Food Process Engineering (UMR GENIAL 1145, AgroParistech-INRA), resulting from the merger between UMR SCALE and UMR Génie Industriel Alimentaire (GénIAl 1145, ENSIA-

[1] See the European projects such as HEATOX et ICARE, among others

[2] Département de Sciences et Procédés des Aliments et Bioproduits, Projet Stratégique 2017-2020.

AgroParisTech), and to which it is linked 2010 UMR Analytical Engineering for Food Quality (IAQA 214). This UMR was chaired by Pr C. Michon until 2016 and then by Dr C. Bonazzi.

Since January 1, 2020: The Paris-Saclay Food and Bioproduct Engineering Research Unit (UMR SayFood 0782, Université Paris- Saclay, INRAE, AgroParisTech), resulting from the merger between UMR GENIAL and UMR Microbiological Engineering and Food Processes (GMPA 782, INRA-AgroParisTech).

The UMR is chaired by Dr C. Bonazzi. Currently on several sites (Massy, Grignon, Paris), all the staff will move to the Saclay Plateau during 2021. The scientific challenges for this new unit aim to rethink the engineering of bio-products and processes to develop the potential of new sustainable food systems (from conception to consumption), this by creating a collective with an integrated and interdisciplinary vision. This research is part of a regional ecosystem which makes it possible to envisage original synergies ranging from agricultural production to distribution and consumption, with outputs towards health or public policies *(fig. 1).*

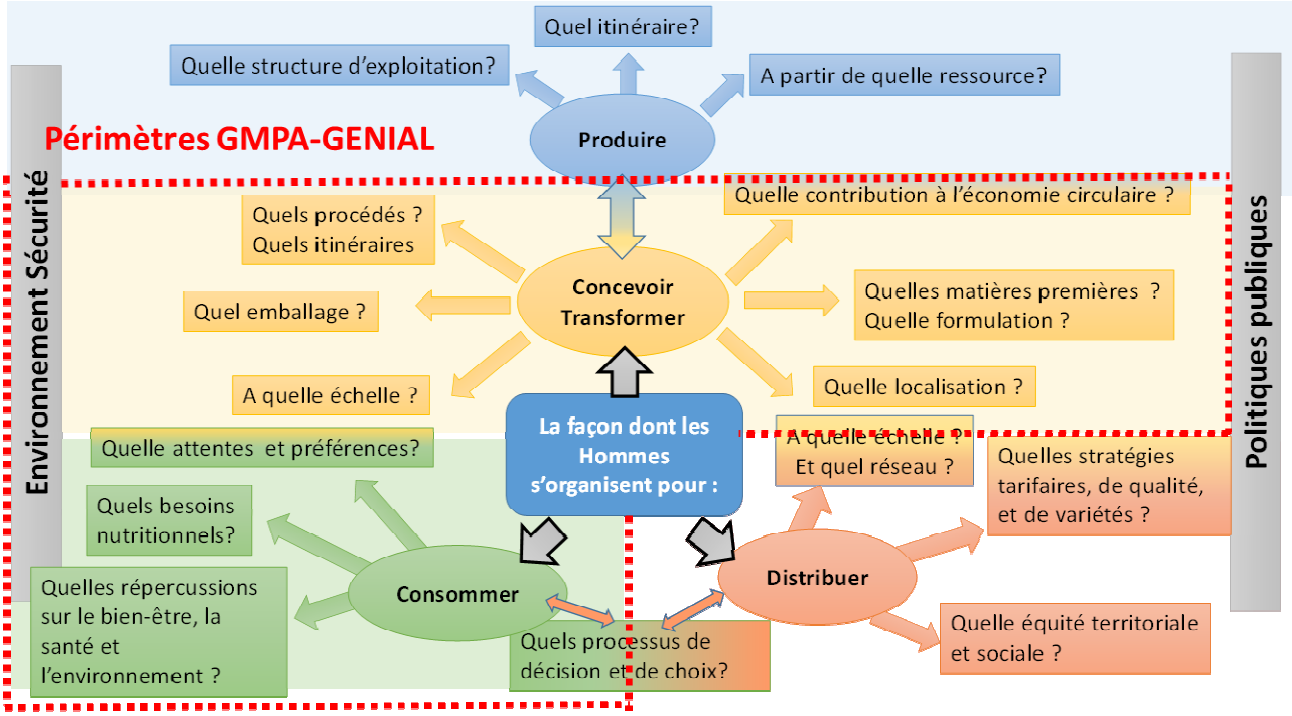


Figure 1: Perimeter of the two Genial and GMPA UMRs which merged in 2020 to give SayFood UMR, According to the HCERES 2018 evaluation report.

The SayFood UMR has 120 permanent staff: 57% of AgroParisTech agents, 32% of INRA agents and 11% of agents from other establishments. It is made up of 22% researchers, 40% teacher-researchers and 38% engineers-administrative technicians. It is structured into five teams: Gépro - product engineering [resp. Pr P. Menut & Dr V. Bosc], CoMiAl - microbial food communities [resp. Dr C. Monnet & Dr S. Helinck], IHAC - human-food interactions for conception [resp. Dr D. Blumenthal & Dr A. Saint-Eve], ProBioSSep - microbiological processes, stabilization, separation [resp. Pr V. Athès & Pr C. Béal] and ModIC - modeling and engineering by calculation [resp. Pr C. Trelea & Dr A. Plana Fattori].

Within this new UMR, **I am attached to the GéPro team** (product engineering - multi-scale construction of functional properties of food and bio-based materials), which aims to develop tools and knowledge for the reasoned construction of the properties of processed products (food products and packaging). The GéPro team was born from the merger of two pre-existing teams: SP2 and Calipro.

The team is focusing its research on the development of original methods, adapted to the study of the dynamics of chemical reactions and transfers within complex food systems subjected to realistic transformation conditions when compared to the industrial conditions. The purpose of this cognitive

approach is the implementation of tools to assist in the design of products and new technological routes, integrating the various components of quality and controlling the environmental impact. My work is at the interface of objectives 1 and 3 of the CaliPro team which will be pursued in the current GéPro team: (1) Understanding and measuring the dynamics of reactions and transfers as well as their coupling in realistic transformation conditions; (3) Predict and control the fate of compounds of interest related to organoleptic, nutritional and safety food quality. **Within the SayFood UMR and GéPro team, I am currently interested in understanding the influence of formulation and process parameters on the generation and degradation of newly formed compounds linked to sensory and safety dimensions, with a view to reason the design of food** *(fig. 2).*

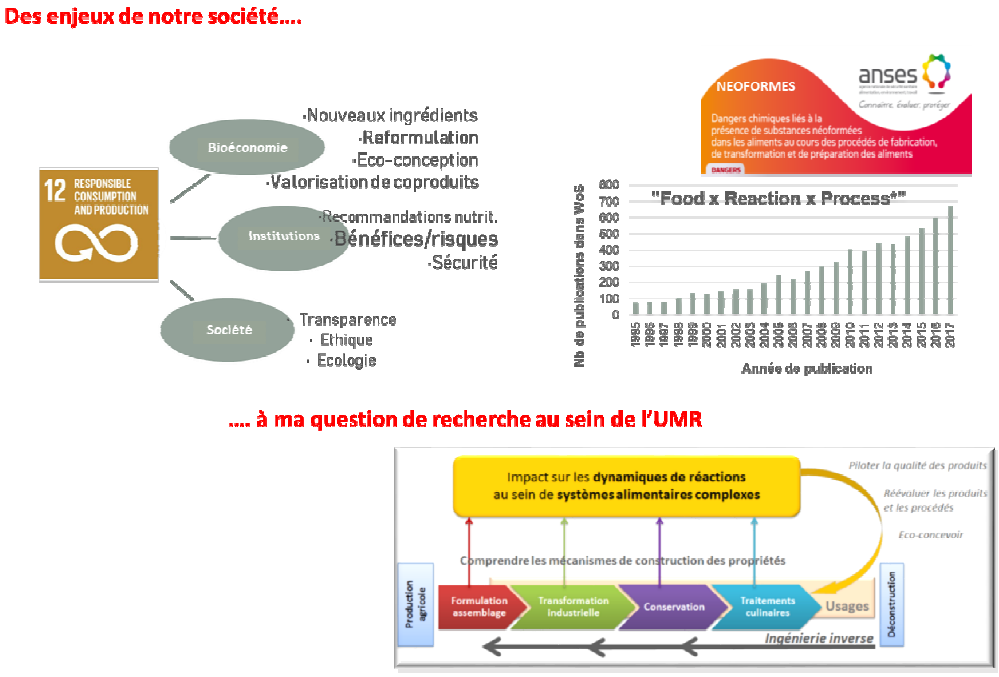


Figure 2: Positioning of my research activities within the UMR, in the scientific context linked to the challenges of responsible production and consumption of the United Nation Sustainability Goals.

Main themes and research activities

General overview: history and trajectory

My research beginnings were in Italy, at the CNR International Center for Mass Spectrometry where I worked on the development of analytical methodologies for monitoring covalent modifications of serum proteins in milk subjected to different heat treatments. As soon as I arrived in France in 2000, I made a major shift in my expertise, in particular by initiating myself into the analysis of aroma compounds. During my thesis at the UMRA of Dijon (currently UMR CSGA), under the supervision of Mrs. E. Guichard, I studied the interactions between food matrix and flavor compounds from a physical-chemical and sensorial point of view. I was looking, on the one hand, at the influence of the structuring of model products on aroma release and, on the other hand at the different levels of texture-flavor interactions in the case of a real food.

I have, however, decided to focus this chapter only on the research activities initiated following my hiring as associate professor at ENSIA (currently AgroParisTech). There, within the UMR SCALE, I had the mission of **developing a new line of research concerning the study of the formation of "newly formed" molecules during thermal processes applied to food.**

During thermal processing such as cooking, a considerable number of compounds can form in foods such as cereal products. Some compounds play an important sensory role when others have an emerging health concern, as these products are widely consumed by people of all ages. It is therefore important and relevant to understand and master their formation in food. I was particularly interested in those newly formed volatile compounds derived from the main thermal reactions such as the Maillard reaction, the caramelization reaction and lipid autoxidation, as well as their interactions, in particular in **starchy products subjected to cooking**.

This thematic involves the understanding of **three main interconnected domains** *(fig. 3)*: (1) newly formed compounds and their links with the determinants of sensory quality (e.g. aromas), (2) the reactivity of precursors and the fate of reaction products, (3) food safety aspects related to potentially toxic newly formed compounds.

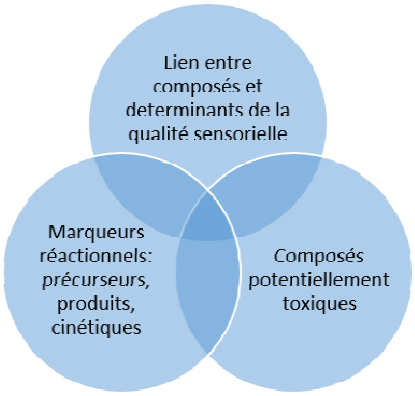


Figure 3: Three interconnected areas of investigation related to my research theme on newly formed compounds

During my activities within the UMR and outside (see map of collaborations in appendix 3), I worked synergistically with colleagues in analytical chemistry, process engineering, sensometrics and chemometrics to explore research fronts around understanding the interconnection between these three areas. *Figure 4* shows the main questions related to the aspects of sensory quality, safety and product engineering when we are interested in newly formed compounds related to cooking. **Thanks to the key contribution of several doctoral students and interns,** I advanced in several stages. I first **developed or optimized numerous analytical methodologies** for monitoring volatile compounds in complex compartments (*fig. 5*, presented in *Axis I*). These methodologies were then used to understand the link between process, formulation and quality determinants through an approach of **formulation engineering** (*fig. 5*, presented in *Axis II*) and then to follow in qualitative, quantitative or kinetic terms the formation of compounds of interest in strict relation with the **reactivity during the cooking processes** (*fig. 5*, presented in *Axis III*).

My personal objective is **to go towards the implementation of a global and transposable approach** of characterization, modeling and validation of the **contributions that reactivity can offer to formulation engineering, through collaborative and interdisciplinary work**. How to identify and exploit the potential of new ingredients / processes while identifying *a priori* potential health risks?

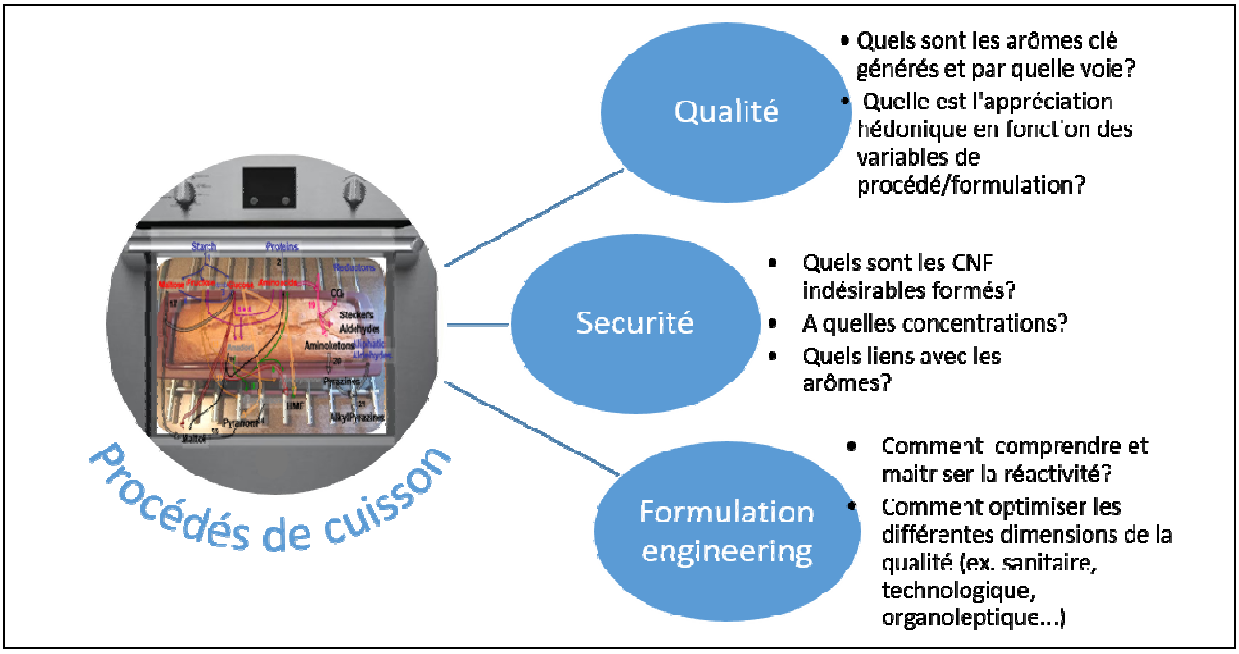


Figure 4: Questions guiding my research activities on the formation of newly formed compounds and the link between process and reactivity.

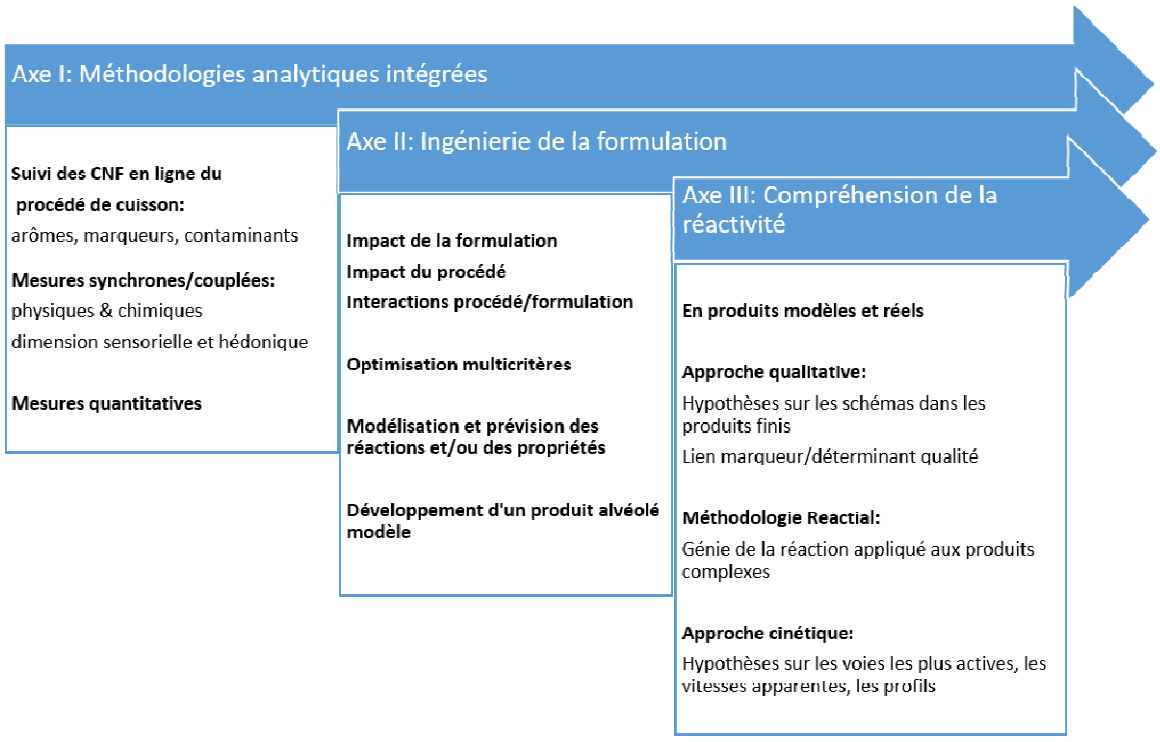


Figure 5: Presentation of my approach as organized in this chapter. The three axes are strictly linked.

Axis I: Development of integrated analytical methodologies for monitoring volatile newly formed compounds (CNFV)

My guiding questions

- How to choose and analyze relevant CNFVs of interest?
- How to follow the CNFV during the cooking process?
- How to dose them in compartments of varying complexity and heterogeneity?
- How to dose the newly formed furanic compounds present in trace amounts?

The challenges of CNFV analysis

The development and optimization of ad hoc chemical measurement methods are essential preliminary steps to work in a relevant way and to tackle, with rigor and ambition, any scientific question related to the quality of food. Analytical development is in fact inseparable from the question to which the food chemist endeavors to answer, despite the fact that I introduce it here as an axis in its own right, for reasons of clarity.

The work on newly formed compounds first raises the question of **identification**. By definition, a newly formed compound is not intentionally added to a food such as an additive or flavoring compound but is generated in situ (Koszucka & Nowak, 2019). We do not know a priori what will be the molecules generated by the reactivity of the food environment and at what concentration we will find them. A second critical point is the **quantification** of these compounds, in particular those which are potentially toxic and which are the subject of risk assessment procedures. With the discovery of the food origin of acrylamide, a lot of effort has been devoted to the development of specific and very sensitive analyzes to quantify the concentrations of these potentially toxic compounds in order to provide robust and numerous data for the assessment of the risk linked to these compounds (occurrence, fate, exposure, even impregnation (https://www.efsa.europa.eu/fr/topics/topic/process-contaminants).

If, then, we want to understand the **reactivity linked to the generation of newly formed compounds**, we must focus on methods which allow us to understand on the one hand the reaction mechanisms and on the other hand the reaction rates. Classical studies on the compounds of the Maillard reaction have only identified a limited number of markers due to the heaviness of the analytical methods applied (Porretta, 1992; Erbersdobler & Somoza, 2007; Rufian-Henares, Delgado- Andrade, & Morales, 2009; Elbashir, Omar, Ibrahim, Schmitz, & Aboul-Enein, 2014) and in particular during kinetic monitoring or the determination of patterns (Whitfield, 1992; van Boekel, 2001; Kocadagli & Gokmen, 2016). Subsequently, thanks to the high-speed and / or high-resolution methods applied to food (eg GC / MS-ToF, GCxGC / MS-Tof, UHPLC / MS-Tof) an exceptional number of compounds could be detected, which has enabled the unambiguous identification of compounds and, in certain cases, enriched the hypotheses on the reactivity of systems (Giri, Khummueng, Mercier, Kondjoyan, Tournayre, Meurillon, et al., 2015; Beleggia, Menga, Platani, Nigro, Fragasso, & Fares, 2016; Pico, Antolin, Roman, Gomez, & Bernal, 2018). However, the separation between analytical approaches dedicated to volatile and non-volatile compounds (i.e. linked in particular to GC and LC analyzes) is still fairly marked because we do not yet have a universal coupling capable of identifying and quantifying everything at once. Analytical progress is nevertheless very rapid and promising in the field of food chemistry, in particular with mass spectrometry imaging techniques (Morisasa, Sato, Kimura, Mori, & Goto-Inoue, 2019).

In particular, in order to be able to follow volatile newly formed compounds (CNFV) throughout their generation in food, the analytical methods must be flexible, have good sensitivity and a wide range of

linearity and be robust in order to be able to adapt to food matrices or complex processes. Ideally, they should be multi-residue, i.e. capable of detecting / identifying / quantifying several compounds in a single analytical procedure. Here we will focus on CNFVs which have different physicochemical properties and which are present at very variable concentrations depending on the type of food and the level of thermal process applied. For example, furan is present at concentrations on the order of ppb, when HMF is present at concentrations on the order of hundreds of ppm in cereal products.

Monitoring of baking aroma compounds in a quick and representative way

Any method of analysis of aroma compounds is confronted with the problem of the r**epresentativeness of the extracts**. Indeed, it makes little sense to seek out the odoractive compounds in an extract which is not olfactory faithful to the starting product. Extraction methods must therefore be optimized by taking into account sensory performance criteria (Priser, Etievant, Nicklaus, & Brun, 1997).

Upon my arrival at ENSIA, I applied **hybrid approaches (instrumental/sensory)** to the study and identification of key odor compounds in different matrices and during different projects, with, each time, the to optimize the extraction step (ACL7, ACL9, ACL10, ACL11, ACL13, ACL14, ACT5, ACT6, ACT7, ACT8, Poster22 to 26).

More specifically, I carried out a sensory optimization of SPME extraction via gas chromatography coupled with direct olfactometry (GC-OD) used during my thesis to identify the **key compounds of the greedy "sponge cake" aroma which is released during baking**. To do this, I coupled hedonic and descriptive sensory tests to evaluate the SPME cooking extracts *(fig 6)*. It was the first time that SPME extracts were evaluated hedonically. We have thus identified at what time of cooking were generated and released the most pleasant smells and also tried to understand what were the descriptors associated with this hedonic appreciation thanks to a free semantic analysis. We were finally able to identify by conventional GC-O 6 main pools of odor-active compounds on the most popular SPME cooking extracts (at 15-25 min of cooking) *(ACL14).*

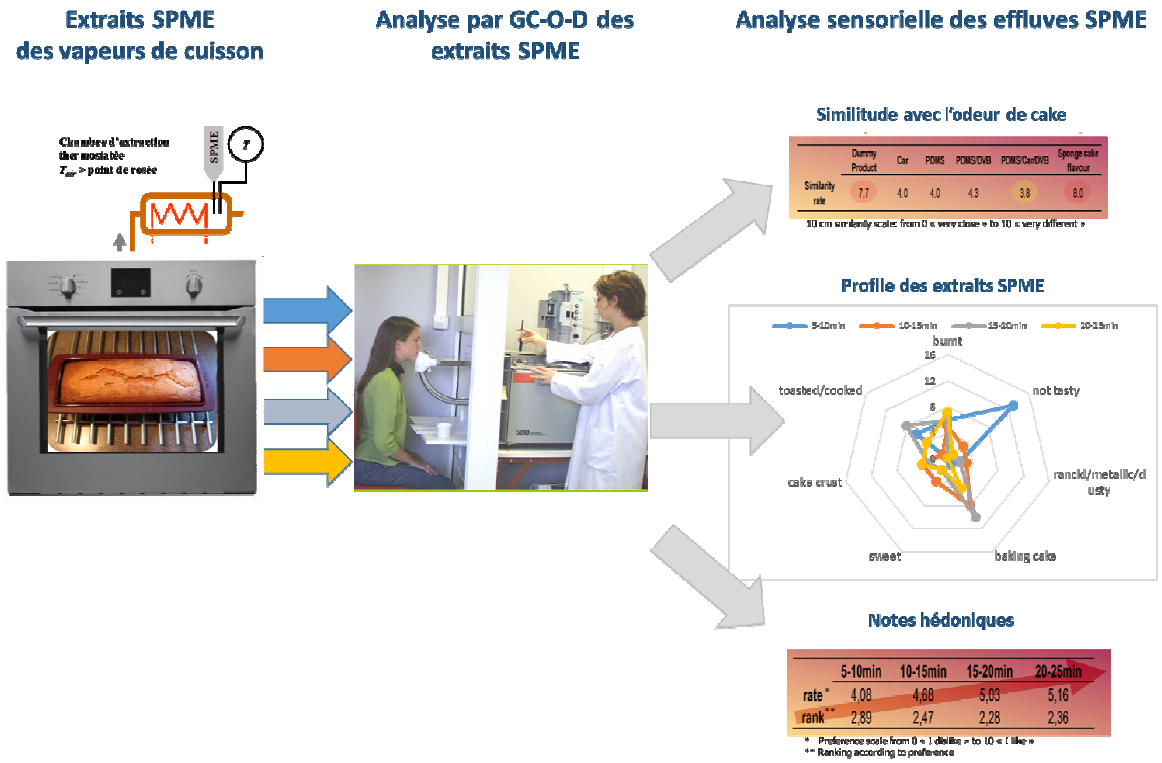


Figure 6: Schematic of the work on sensory & analytical optimization of the SPME extraction of key compounds of the gourmet aroma of "sponge cake" which is released when sponge cake is cooked.

Development of online extraction of a baking operation

Dynamic SPME extraction

To be able to achieve such results, we had developed a first system for extracting cooking vapors using **dynamic SPME in line with a baking oven** sized specifically for a cereal matrix (sponge cake). The vapors emitted by the sponge cake during cooking are sucked in at a constant rate and conveyed to a trapping cell maintained at a constant temperature. The extracts were then analyzed "offline" by GC / MS. The extraction during the entire cooking time made it possible to have a global overview of the molecules generated and released during cooking, when extraction at different cooking intervals (0-5 min, 5-15 min, 15-25 min) provided access to information on the generation and release of aromas at the various stages of chemical and structural transformation of the dough. A very large number of volatile compounds generated by different reaction pathways could thus be identified, among them Strecker's aldehydes such as 3-methylbutanal (chocolate odor) and lipid oxidation products such as oct-1-en-3-ol (mushroom odor) *(ACL14).*

A significant **optimization work** on dynamic extraction made it possible to obtain the most suitable SPME extraction parameters (type of SPME fiber, temperature and extraction rate) for a global monitoring of volatile compounds from cooking vapors, from the point of view of selectivity, sensitivity and repeatability. For example, we have shown that the optimal extraction conditions are not the same for the different compounds present in cooking vapors. Response surface modeling on a set of experimental data obtained from cooking extracts of sponge cake, showed that the low extraction rates (1 $Lmin^{-1}$) were favorable for the extraction of the most volatile compounds (eg 3-methylbutanal), when the highest flow rates and temperatures in the experimental design were favorable for the extraction of the least volatile compounds such as HMF *(fig. 7)*. The choice to spike the sponge cake with a known and constant concentration of standard volatile compounds has allowed us to have specific access to the performance of online extraction, freeing us from the variability linked to the generation of compounds newly formed by the baking process.

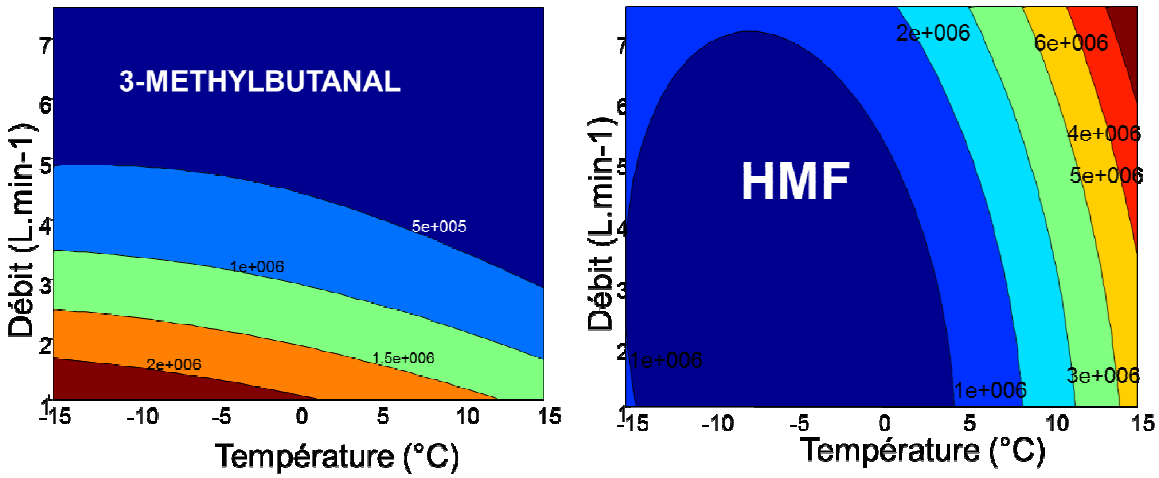


Figure 7: Response surfaces of 3-methyl butanal and of HMF extracted by dynamic SPME and analyzed by GC / MS in SIM mode. The red areas are most favorable for the dynamic extraction of the compound. According to M. Maire's defence (Mast5).

These first results showed us the potential of such an approach from the point of view of the richness in extracted compounds and the relevance for the kinetic monitoring of many reaction markers which follow different profiles according to their reaction origin. These studies have also shown that optimal parameters are identifiable and specific to the experimental objective pursued (i.e. monitoring of odorants, qualitative screening, kinetic monitoring of some markers).

Monitoring the dynamic SPME of a baking oven online seemed to us the ideal method for understanding the generation and release of CNFVs. This approach has the advantage of not disturbing the product during cooking and of allowing the monitoring of many compounds without processing the sample *(ACL14)*. Another advantage of this dynamic method is to extract CNFVs with very different physicochemical characteristics, which made it possible to simultaneously detect very polar compounds like HMF and very volatile like 2-methylpropanal throughout the cooking.

Analytical developments continued with, in particular, the adaptation of the trapping system for quantitative purposes using an extraction method using adsorbent tubes coupled with TD-GC/MS.

Figure 8 illustrates the **different stages of development and validation of the online monitoring methodology of the CNFVs during successive projects.**

To do this, I was keen to **strongly involve doctoral and master's students** in this process of developing innovative methods in order to train them in experimental rigor and critical analysis for the interpretation of data and thus prepare them for their future profession as researchers or scientific managers.

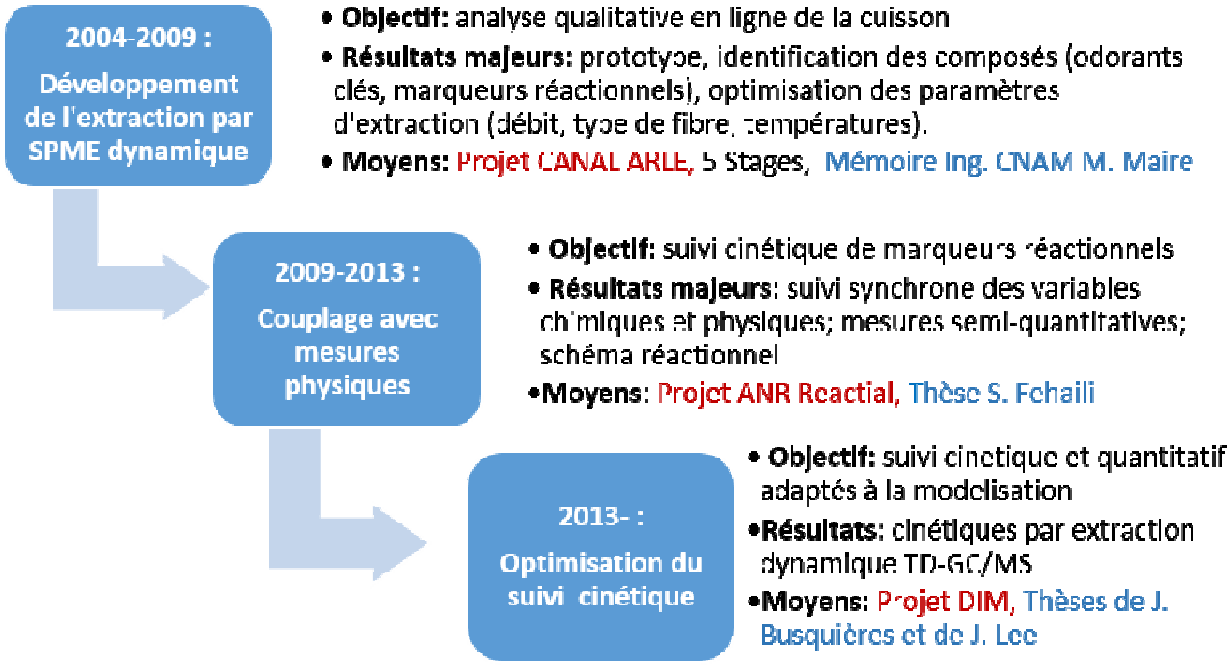


Figure 8: Different stages in the development of the online monitoring methodology of the CNFVs.

Coupling CNFV extraction with physical measurements during cooking: development of the Reactial instrumented oven

To be able to go further in the kinetic monitoring of reaction markers, we have developed an instrumented oven for the **synchronous monitoring of chemical** (reaction markers such as CNFV and non-volatile precursors) **and physical measurements** (temperatures, humidity) of the baking. This development required many areas of expertise (analytical chemistry, process engineering, industrial design) who worked together as part of the Reactial project and the **thesis of S. Fehaili** *(Th1)*. The originality of this project was **to develop in a global way a cooking and measurement tool adapted to the reaction environment under study**, by integrating from the start the desired performance criteria (sensitivity, reproducibility, speed of acquisition) as a function of the analytical and modeling constraints.

The salient results of this study are reported here and are gathered in the article ACL12 (Annex 1)

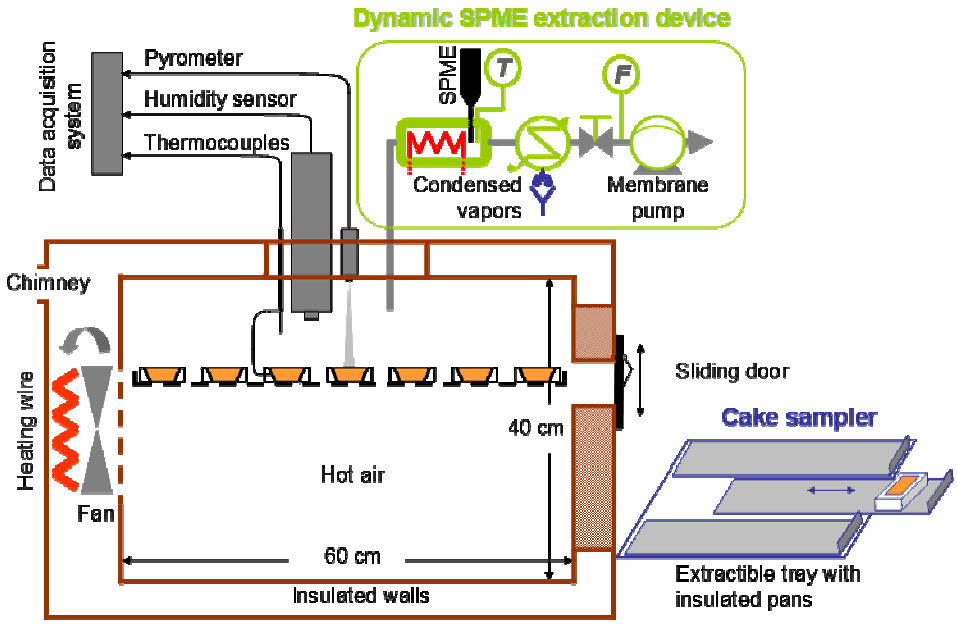


Figure 9: Diagram of the Reactial oven for monitoring the CNFV during cooking. According to the thesis of S. Fehaili *(Th1)*.

The latter in particular has been optimized in order to extract and **follow kinetically and semi-quantitatively selected volatile markers** including 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one (DDMP), acetic acid, formic acid, furfural and HMF. Repeatability, linearity and robustness could be determined and validated for the needs of the study. We also showed that the on-line extraction of CNFV from this oven did not disturb the cooking process and that, in the case of HMF, the release profile obtained by dynamic SPME followed the concentration profile obtained on the matrix *(ACL12)*.

This work therefore made it possible to develop a tool (the instrumented oven) for the synchronous acquisition of chemical and physical kinetic data adapted to a reaction engineering approach via the use of online extraction by dynamic SPME. This extraction method, however, posed limitations in sensitivity for short baking times and in robustness during manual handling. The partition of volatile compounds between the vapors sampled in the extraction cell and the small volume of SPME fiber polymer proved to be a difficult parameter to evaluate in order to extract quantitative and reproducible information from one batch of fibers to another.

Development of online extraction coupled with TD-GC / MS

To overcome the limitations mentioned above, the on-line extraction device has been optimized by **replacing the dynamic SPME extraction cell with a device using sorbent tubes analyzable by thermosorption (TD)** coupled with GC / MS *(fig. 10)*, during the **thesis of J. Bousquières** *(Th3)*. This new device is very simple and robust (stainless steel material, deactivated glass connectors) and simplifies the handling of extractions during cooking. The large quantity of adsorbent (relative to the SPME) and the geometry of the assembly make it possible to extract all of the volatile compounds from a known volume of vapor withdrawn during baking while being freed from the dynamic equilibria of the online SPME cell. These characteristics make this device particularly interesting for kinetic studies where it is required to have a large range of linearity and flexibility (sensitivity, reproducibility, responsiveness) with the possibility of accessing concentrations.

For this study, Air Toxics type tubes composed of two beds of adsorbents (Carbosieve SIII and Carbopack B, Perkin Elmer, USA) were selected for their ability to extract compounds from 3 to 12 carbons.

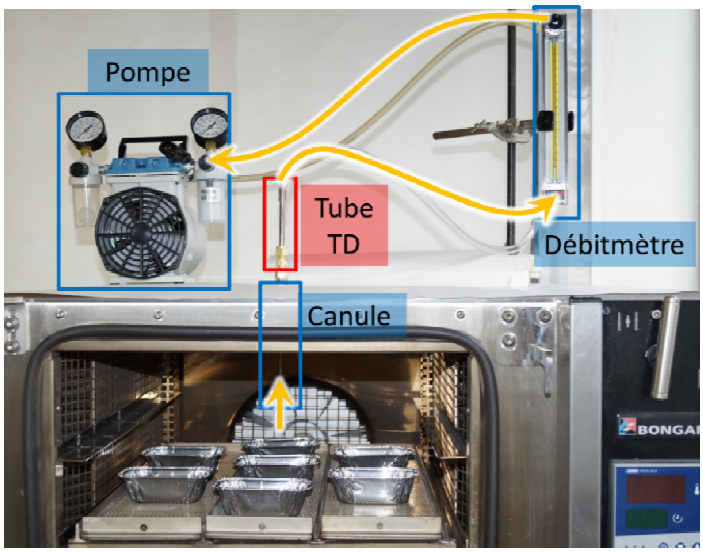


Figure 10: Diagram of the extraction assembly using on-line adsorbent tubes suitable for the Reactial baking oven. According to (Poster12).

The extraction of 12 volatile compounds tested over very short cooking intervals (4 min) made it possible to assess the ability to generate close, numerous and reproducible kinetic points. The potential of this method for kinetic monitoring of cooking reactions has been explored in an article which has just been accepted *(ACL1)*. It has thus been shown that it is possible to follow CNFV over a wide range of cooking times and concentrations and for numerous points of kinetics.

The salient results of this study are reported here and are gathered in the article ACL1 (Annex 1).

Quantitative determination of volatile markers by TD-GC / MS

When the scientific need is to identify reaction pathways by applying a kinetics modeling approach, it is crucial to quantify the reaction marker CNFVs because only the measured quantities of marker can make it possible to build a database usable by modeling.

To do this, we have undertaken substantial work to develop an original method for quantitative monitoring of CNFV by online extraction and TD-GC / MS analysis, thanks in particular to the **thesis of J. Lee** *(Th5)*. Figure 11 summarizes the experimental strategy developed. The concentrations of 10 CNFV were measured by TD-GC / MS in cooking vapors using calibration curves and two stable isotopes used as internal standards (furfural-D4 and 2,5-dimethylpyrazine-D4). The idea here is to spike each sampling tube with the same amount of internal standards used for the calibration tubes. In this way, it is possible to obtain the concentration of the analyte trapped in the adsorbent tube expressed in moles per volume of extracted air ($mol \cdot Lextracted\ air^{-1} \cdot g\mathrm{dm}^{-1}$).

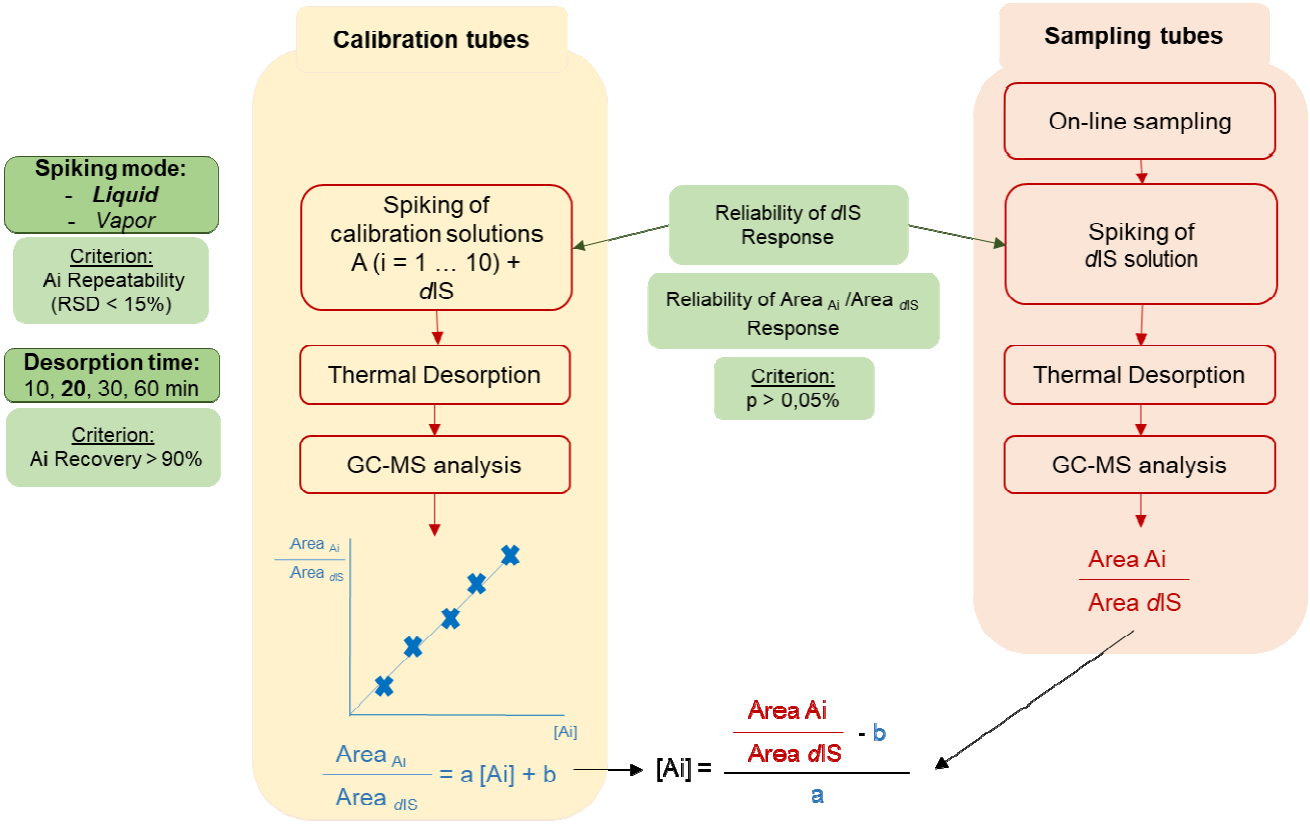


Figure 11 : Analytical strategy applied for the development and validation of the quantitative TD-GC/MS method: the analytical steps are circled in red while the parameters tested are in dark green and the performance criteria chosen for the optimization are in light green. Publication in progress.

The use of deuterated internal standards has the advantage of verifying the variability due to the analytical protocol and avoid the mass detector variations over time. This quantitative method represents a real **methodological advance for the team** because, for the first time, it was possible to quantify the volatile markers by online sampling of baking vapors with criteria established upstream for stoechio-kinetic modeling. The results are being published.

Quantitative determination of other markers for modeling

However, to be able to carry out modeling studies of reaction kinetics, the data on the CNFVs are not sufficient. It is just as essential to measure the precursors and key intermediates of reactions over time.

To do this, in parallel with the determination of CNFV by TD-GC/MS, other methods for the determination of precursors and intermediates have been developed using UHPLC coupled to different detectors (DAD, CAD, QToF-MS), recently acquired in the laboratory. Thanks to this work carried out within the framework of J. Lee's PhD thesis, it was thus possible to **quantitatively follow 20 selected markers (10 volatile markers and 10 non-volatile markers).** We have also chosen to dose 2 CNVFs (furfural and HMF) in both the solid product and the vapor phase in order to have an estimate of the partition between the two compartments. The application of these methods and the main results will be presented in *axis III*. *Fig. 12* schematically shows the overall analytical strategy carried out for the determination of the 20 reaction markers during the cooking of a model product.

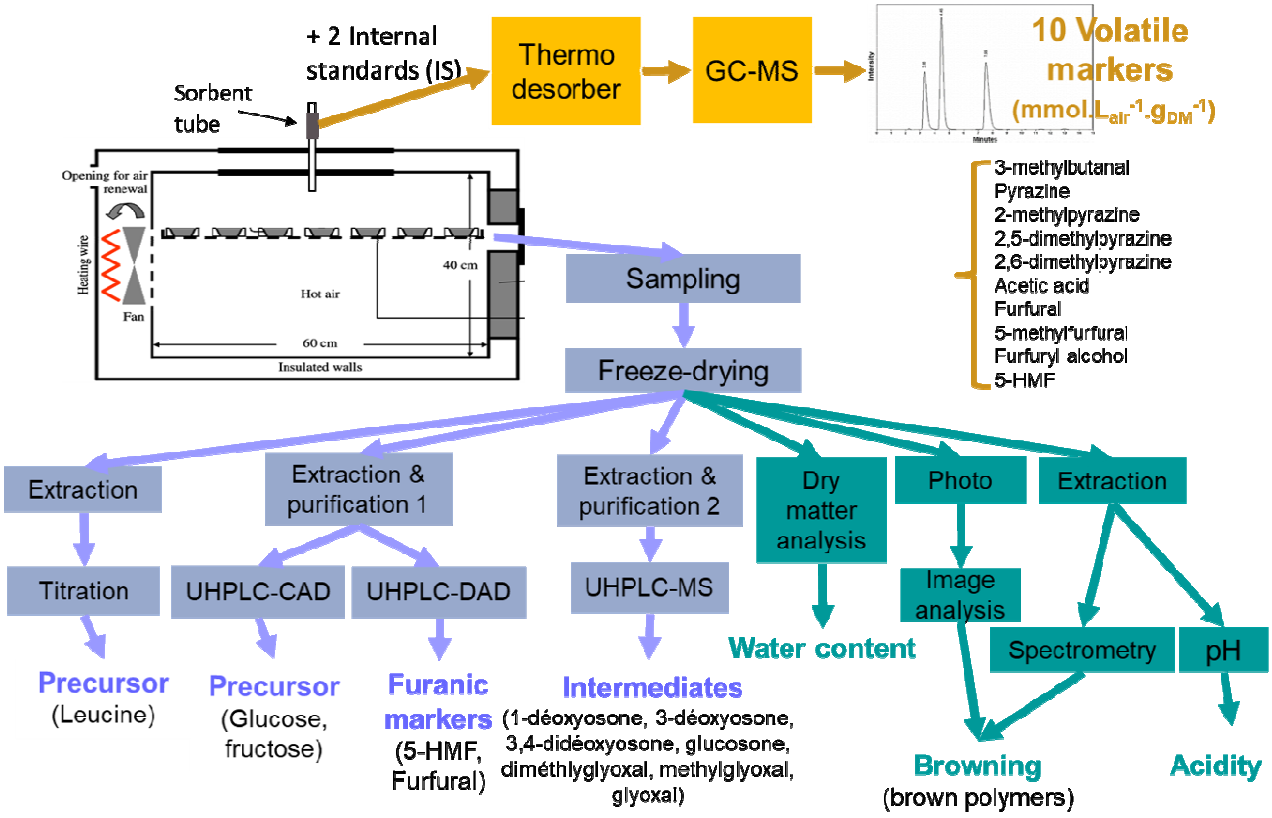


Figure 12: Analytical strategy of 20 volatile and non-volatile markers for monitoring reactivity in a model sponge cake. According to (Oral1).

Method development and optimization o for measuring furan by isotopic dilution in food matrices of increasing complexity

Furan is a Class 2 contaminant of IARC. It can form in several foods following various sterilization/cooking processes (Crews & Castle, 2007). This compound has no olfactory impact *per se*. It is formed in trace amounts and is highly volatile (T_b: 31°C). An EFSA report published in 2017 highlights the risk of food exposure to this CNFI *(Knutsen, Alexander, Barregard, Bignami, Bruschweiler, Ceccatelli, et al., 2017).* All these characteristics and the presence of factors highly favorable to its formation via cooking processes, make it a point of major interest by the scientific community working on undesirable CNFVs.

For this trace compound, it is important to have sensitive assay methods, validated and adapted to the different food matrices. If in literature there are methods of dosing commercial products (e.g. canned baby products), the dosage of this compound following cooking processes (e.g. household or industrial operations) is much less studied because of the analytical challenges it poses (high volatility, interactions with the matrix, toxicity, control of cooking parameters).

I therefore had the objective of monitoring and quantifying furan in starchy products of wide consumption (subjected to baking). To do this, I supervised the optimization and validation of methods based on headspace (HS) extraction coupled with GC/MS analysis in SIM mode adapted to the different matrices and processes under study, during several successive projects, notably ANR projects Dominove and Satin and during **M. Cepeda's thesis** *(fig. 13).*

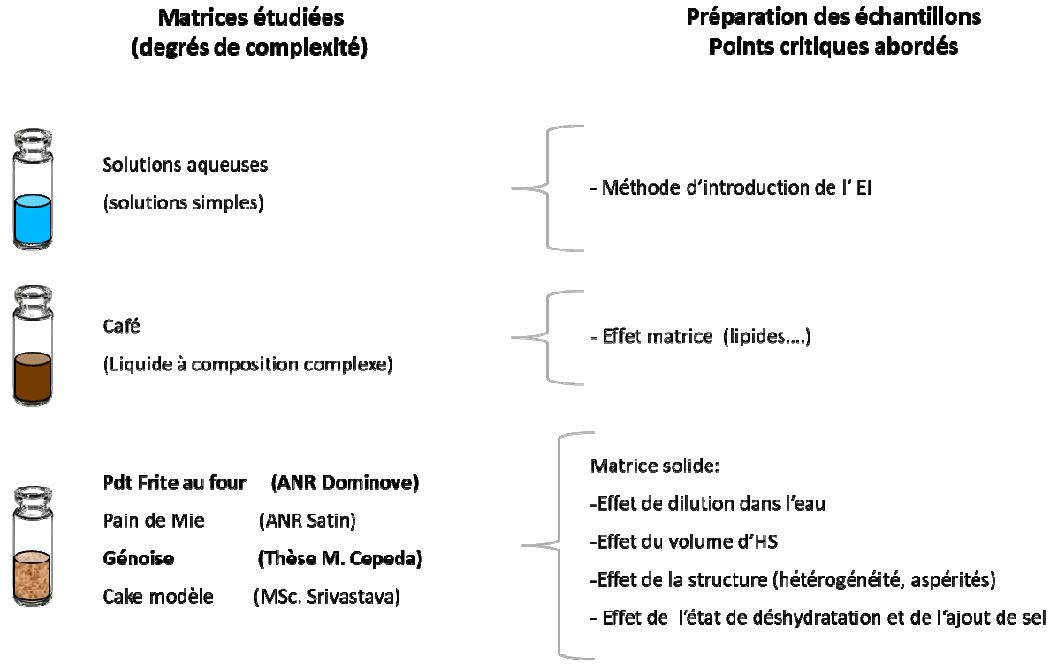


Figure 13: Complexity of matrices and corresponding analytical challenges. Of the different projects cited on starchy matrices, only the example on the sponge cake will be developed in this section.

Multi-criteria optimization of furanic compounds extraction by HS Trap

Knowing the concentration of furan simultaneously with that of other furanic compounds is essential to understand their simultaneous generation in cooked cereal products and to develop strategies for reducing / eliminating unwanted CNFVs, especially because most of them are linked to flavor generation.

To do this, we developed a method for the **simultaneous quantification of furan and furfural by HS trap** in a widely consumed cereal product (sponge cake type) during the **PhD thesis of M. Cepeda Vasquez** *(Th4)*. The simultaneous quantitative analysis of these furan compounds is a challenge because they are found in different concentrations (ppm, ppb) and have distinct physicochemical properties.

To achieve this, we used **advanced chemometrics tools** (Optimal Design of Experiments, O-DOE) to determine the effects of instrumental and preparation variables on the extraction of furan and furfural by HS trap. Then we optimized the conditions for implementing this method thanks to the desirability function. *Figure 14* shows the analytical strategy that we have implemented. During this systematic study, we took into account 4 instrumental variables (X1 to X4, *fig. 14*) and two variables related to the preparation of the sample (X5, X6, *fig. 14*). The latter were selected following the results of previous work on the optimization of the HS extraction parameters mentioned above.

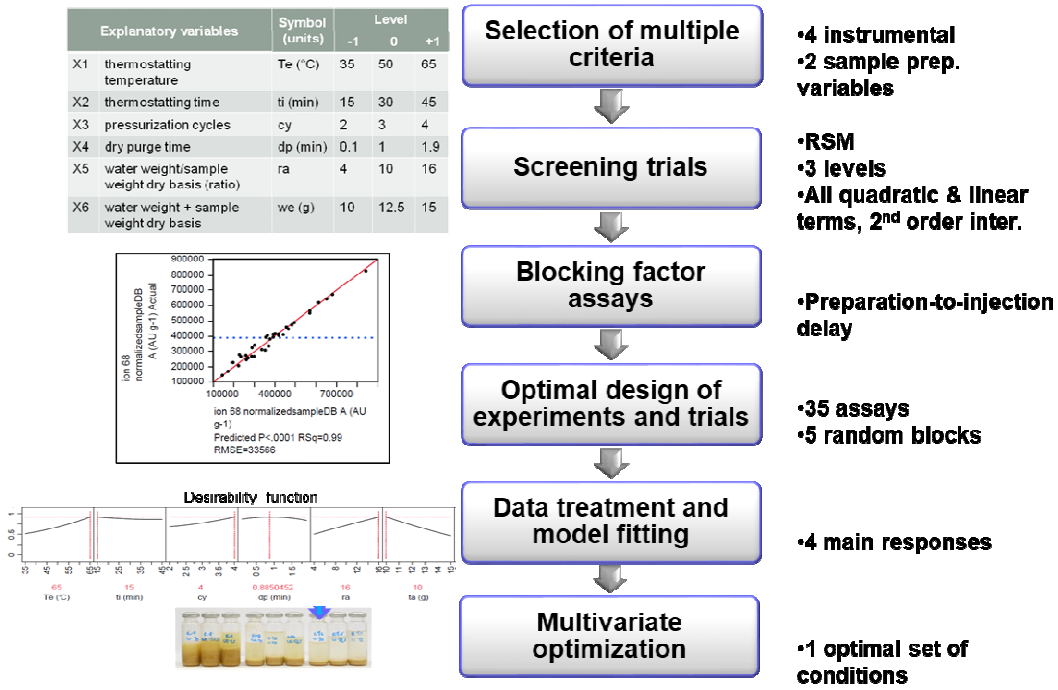


Figure 14: Optimization strategy for the simultaneous quantification of furan and furfural by optimal design of experience and desirability function. Adapted from the thesis of M. Cepeda Vazquez (Th4).

The salient results of this study are reported here and are gathered in the article ACL5 (Annex 1).

The extraction temperature (Te) and the water/sample quantity ratio (ra, on a dry basis) exert linear effects on the furan and on the d4-furan. However, when studying the furan/d4-furan ratio, some interesting behaviors are revealed. Thus, as shown in *Fig. 15*, the extraction temperature has neither a quadratic effect nor a linear effect on the furan/d4-furan ratio. This result is very interesting because it shows that under our experimental conditions no generation of furan in situ is induced up to 65°C, unlike the previous results for other food products and methods. In addition, the ratio (ra) has a quadratic effect on the furan/d4-furan ratio. This means that in the interval studied, the heaviest isotope is significantly better extracted than the unlabeled compound when the factor ra increases; therefore, it is essential to establish and control the water to sample ratio, especially when isotopic dilution is used as the quantification method.

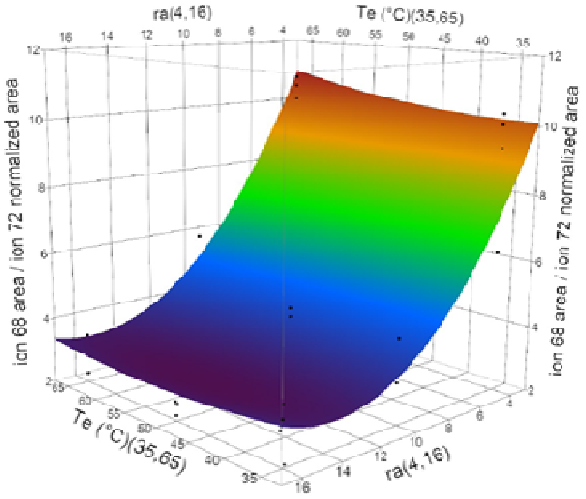


Figure 15: Response area for the ratio furan/d4-furan. Response [ion 68 (furan) area / ion 72 (d4-furan) area] in function of the thermostat temperature (Te) and of the water to sample ratio (ra, dry base). According to ACL5.

Multi-criteria (4 extraction and analysis variables) and multi-response (furan, furfural, d4-furan, d4-furfural) optimization, performed on the basis of a desirability function, made it possible to find the optimal analytical conditions.

The quantitative HS trap-GC/MS method was then validated and the performance characteristics of the optimized method are summarized in table 1. Low intra- and inter-day variability was achieved for both furan and furfural. Good linearity was observed in the validation domain. This was evaluated for both aqueous and sponge cake samples, and was therefore defined as the linearity domain. As far as sensitivity is concerned, this method is very effective, making it possible to quantify traces of furan and furfural (ppb) in a solid and complex product.

Table 1: Validation of the method of simultaneous quantification of furan and furfural. Based on (ACL5).

Validation criteria	furan	furfural
Repeatability (Intraday), RSD (%)	1.9-3.3	2.0-2.6
Intermediate precision (Interday), RSD (%)	4.0	4.3
Linearity range (ng/g_{sample}, dry basis^{-1})	0.99-300	41.1-9000
LOD (ng/g_{sample}, dry basis^{-1})	0.50	10.2
LOQ (ng/g_{sample}, dry basis^{-1})	0.99	41.1

Additional tests using the same method on other sponge cake samples have shown that, although slight matrix effects are observed for furan and d4-furan, furan and furfural still behave similarly to their corresponding isotopic standards. These results confirm that, under our optimized HS-Trap analysis conditions, an isotopic dilution is sufficient to overcome the matrix effects, avoiding having to carry out the method of standard additions which takes an enormous amount of time for each sample, as we have experimented in a previous work which was not presented here.

By its performance and thanks to the validation step, this method was applied to other cereal matrices with variable moisture and fat contents having very variable levels of furan and furfural concentration. In addition, this method has been adapted for the semi-quantitative analysis of 12 other flavor markers and reaction markers.

This analytical strategy is interesting because it can be transferred to other types of problems in optimizing the dosage of newly formed compounds.

Highlights of Axis I

We have developed and validated methods adapted to different analytical issues (monitoring of compounds of interest, quantitative trace analysis, kinetic analysis) and in particular:

1. We set up the online monitoring CNFV during process, applied to the case study of a cereal product baking
    a. For sensory evaluation of vapors
    b. For quantitative monitoring of volatile markers
    c. For synchronization between chemical and physical measurements for kinetic studies
2. We have developed and validated the dosage of furan compounds present in trace amounts
    a. in complex starchy matrices
    b. by reflecting on the matrix and the relevance of the analytical choices

Professional development and valorization

3. I have developed expertise on online measurements and on quantitative measurements of CNFVs

4. I have trained 5 doctoral students and 5 master students through research by involving them in the development and validation of original analytical methods.

5. I valorized the main results with 6 peer-reviewed articles, 2 publications of conference proceedings and 13 posters.

Axis II: Study of the links between manufacturing process (process, formulation), reactivity and quality determinants

My guiding questions

- What is the link between occurrence of CNFV and thermal reactions during a cooking process?

- How to identify and optimize the most influential parameters of formulation and process for controlling the content of newly formed compounds?

- What levers for the design of sensory and safety quality?

Identification of CNFVs of interest, main generation paths and interactions

Sponge cake as subject of study

The sponge cake is a soft cake obtained by baking a liquid foam obtained by beating the eggs with the sugar in which flour and a little fat are incorporated. Different recipes exist depending on whether the process is closer to an artisanal production (fresh eggs, sucrose, and flour mainly) or an industrial product of long conservation (powdered eggs, fat, leavening powders, glucose syrup and preservatives) *(Monnet, Laleg, Michon, & Micard, 2019).*

This product was chosen because it makes it possible to investigate many interesting questions: by its ingredients it contains many precursors of the main thermal reactions. The high percentage of eggs distinguishes it in particular from other oven cereal products. The modification of some of these ingredients (nature of the sugars, composition of the fat) makes it possible to explore the main reactions that occur during making and cooking. Its structure develops during beating and consolidates during cooking. The mass and energy transfers that take place during cooking are inherent in the alveolar structure of the product. The sponge cake is made up of two macroscopic compartments: the crust (brown color) and the crumb (light color) at the level of which the thermal reactions advance at different speeds, due to different local temperatures and humidity.

In my first works, carried out as part of the CANAL-ARLE project and the COST 927 action, I was able to identify many CNFVs that are formed in this type of product. In particular, furan compounds (e.g. 5-hydroxymethylfurfural and furfural), many Strecker's alhedydes (e.g. 3-methylbutanal and benzaldehyde) and alyphatic aldehydes (e.g. hexanal and nonanal). Among the CNFV we have identified the key compounds of the aroma of " baking genoise", such as 3-methyl butanal and 2,5-dimethylpyrazine using the GC-OD technique previously illustrated in the *axis I*. These odor-active compounds were detected on the most appreciated cooking fractions (between 15 and 25 min of baking), *(ACL14, ACT 7, Poster 26, Oral 6).*

The salient results of this study are reported here and are gathered in the article ACL14 (Annex 1).

The generation of these compounds was followed both on the product (dough and cakes baked at three increasing times) than in the cooking vapors *(fig. 16)*. The CNFVs identified come from different reaction pathways such as the Maillard reaction (RM), the degradation of Strecker (DS), caramelization (C) and lipid autoxidation (OL), as shown in the simplified diagram that we have developed based on the available literature *(fig. 17)*. RM occurs between the carbonyl groups of reducing sugars and the -NH2 functions of amino acids, peptides and proteins. C is a direct breakdown of sugars. These two reactions result in common intermediates (deoxyosones) and furan compounds. During DS, free amino acids react with deoxyosones from the RM and C pathways to form Strecker's aldehydes and aminoketones. The latter can cyclize and subsequently form pyrazines. The lipid autoxidation, radical chain reaction (initiation with formation of free

radicals, propagation and finally termination with formation of non-radical products) is at the origin of the aliphatic aldehydes detected here as well as the products of their cyclization (2- pentylfuran).

It is interesting to note that, unlike the RM and C markers, the CNFVs of lipid oxidation are also detected in the dough and at the very start of baking *(fig 16),* suggesting an oxidation started before baking.

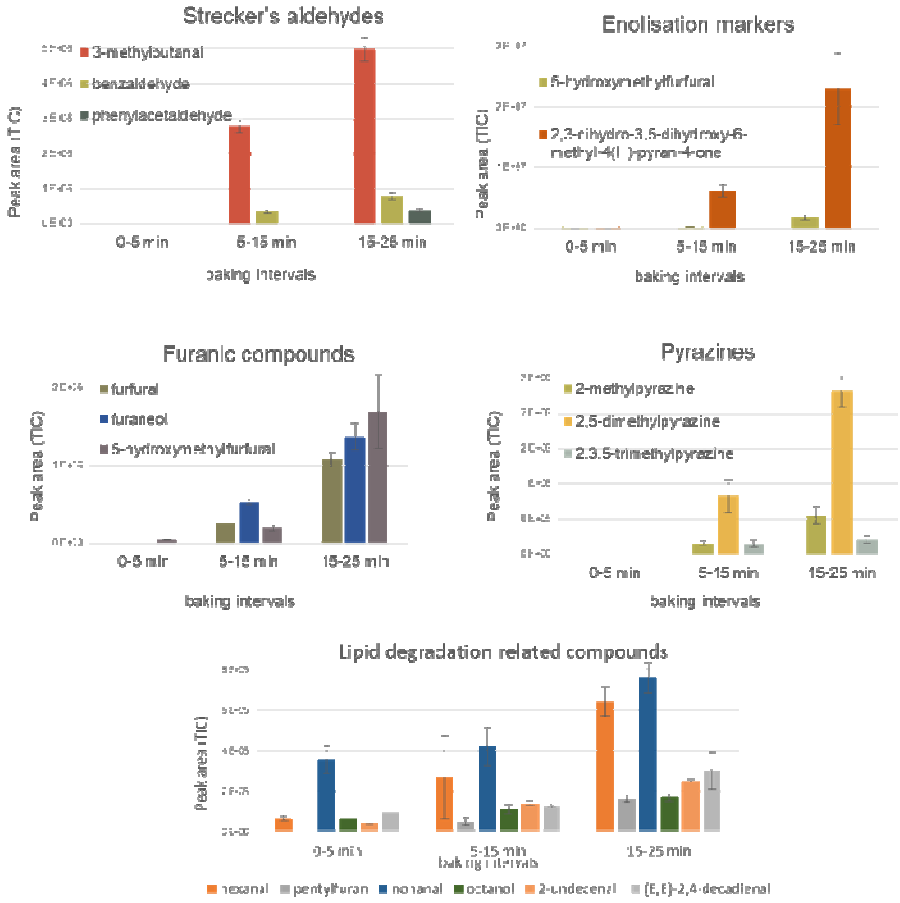


Figure 16: CNFV monitoring during baking by dynamic SPME extraction. Based on (ACL14).

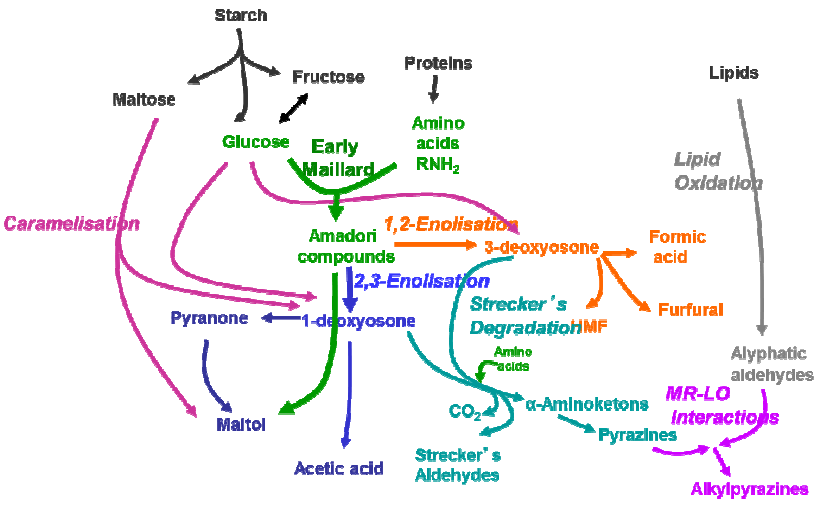


Figure 17: Simplified diagram of the main CNFVs generation in a cake type product. The different reaction paths are illustrated by different colors. According to (Oral6).

Following these encouraging results, I wanted to study under what formulation conditions (reactive ingredients) the formation of CNFV was amplified or, on the contrary, inhibited and if interactions between the Maillard reaction and the other reaction pathways were favored in this complex reaction medium. Indeed, the change of ingredients can modify the content in precursors or catalyzers of the main reactions occurring during the manufacturing stages of the product.

Reactivity of sugars, impact on the profile of CNFV

First of all, I compared the reactive potential of three different sugars with regard to the formation of CNFVs: sucrose (S) – a non-reducing disaccharide–, glucose (G) – an aldose – and fructose (F) – a ketose. These sugars were used in equi-mass quantities in 3 formulas subjected to the same preparation and cooking processes (170 ° C for maximum 30 min) during the M2 course of E. Machado-Maturana *(Mast7).*

Figure 18 shows the evolution of the main CNFVs in each formula as a function of cooking time. All Maillard, Caramelization and Strecker's compounds are detected after 10 min of cooking and their quantity increases with cooking time. In general, whatever the cooking time, formula F is the richest in volatile compounds and formula S the least rich (F> G> S). In formulas based on reducing sugars the Caramelization and Maillard reactions are apparently faster, which is also confirmed by a higher level of browning measured for the same time / temperature scale.

Sucrose requires prior hydrolysis before reacting in Maillard and caramelization pathways, which delays browning. However, it is interesting to note that the sucrose-based formula, although overall less rich in CNFV, is the one for which the pyrazines (eg methylpyrazine and 2,5-dimethylpyrazine, key odorous compounds of sponge cake) are found in more quantity high.

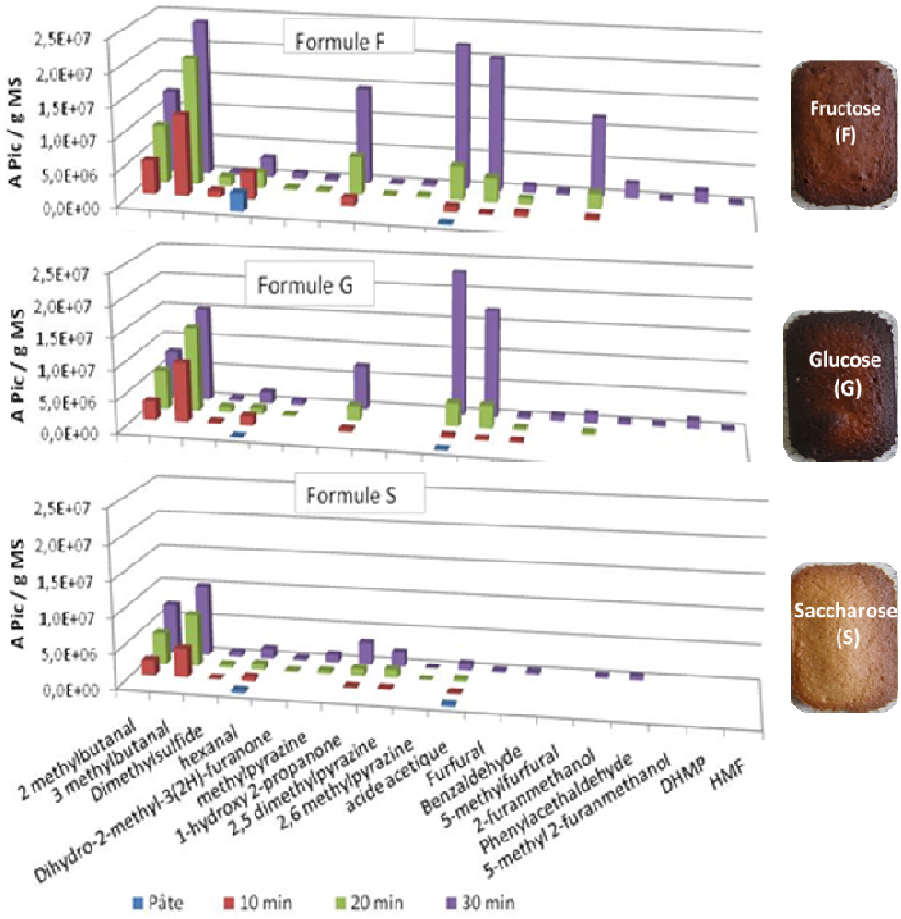


Figure 18: Evolution of the main CNFV for 3 formulas based on different sugars (F: Fuctose, G: glucose; S: sucrose) according to the cooking time at 170 ° C. HS-SPME extraction with DVB / Car / PDMS fiber. According to (Mast7).

This result seems to indicate that the formation of pyrazines is disadvantaged in formulas with highly reactive sugars such as F and G. We can hypothesize that the aminoketone which is formed concomitantly with Strecker's aldehydes could enter reactions other than cyclization to pyrazines, such as, for example, deamination with the formation of new reductones *(Niquet & Tessier, 2007)* or the formation of 1-hydroxy-2-propanone which is in fact found in greater quantity in formulas F and G *(Whitfield, 1992).*

Reactivity of lipid ingredients with regard to the formation of lipid oxidation products and identification of key steps in the sponge cake manufacturing process

If MR and C require high activation energy and occur mainly during heat treatments, LO requires low energy. In addition, in several cereal products, the enzymatic mechanisms of oxidation should not be underestimated, especially in the presence of active lipoxygenase *(Frankel, 2005).*

I therefore wanted to direct my research to understand how the **fat composition**, and in particular the content of Polyunsaturated Fatty Acids (PUFA), can favor the appearance of lipid oxidation products in this type of cereal product and at **what moment of the manufacturing process** the OL is likely to occur.

Five formulations were developed during the **internship ing. CNAM by M. Maire** *(Mast5)* by changing the nature of the fat or the composition of the egg, so as to vary the rate and degree of oxidizability of polyunsaturated fatty acids (PUFA) provided by these ingredients. A multivariate analysis (FDA) made it possible to **discriminate the formulas as a function of the increasing degree of oxidability of the fat used** *(fig. 19B).*

The salient results of this study are reported here and are gathered in the article ACL 8 (Annex 1)

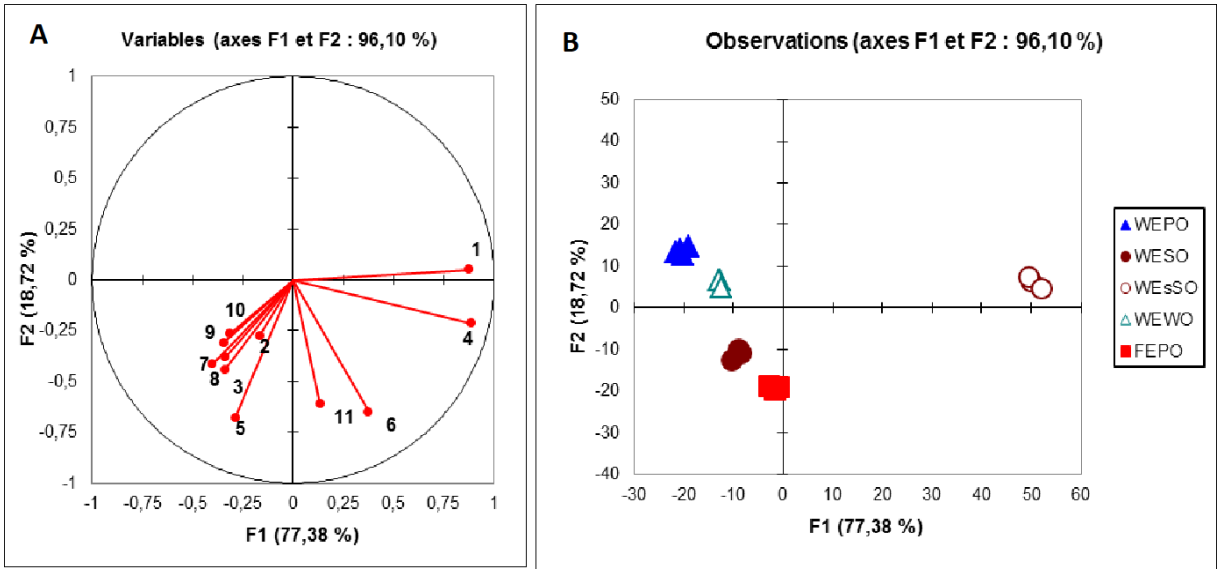


Figure 19: FDA analysis on oxydation aldehydes: 1 : Hexanal - 2 : Heptanal - 3 : Octanal - 4 : (t)-2-hepténa l - 5 : Nonanal - 6 : Octadécanal - 7 : Décanal - 8 : (*t*)-2-nonénal - 9 : (*t*)-2-décénal - 10 : 2-undécénal - 11 : (*t,t*)-2,4-décadiènal. FEPO: reference formula with egg yolk and palm oil. WEPO: formula without yolk and with palm oil; WESO: formula without yolk and with sunflower oil; WEsSO: formula without yolk and with stripped sunflower oil; WEWO: formula without yolk and without palm oil. Based on (ACL8).

It is therefore clear that the presence of endogenous tocopherols has a strong protective effect against the oxidation of PUFAs in sponge cake.

This work also allowed us to observe the **role of egg yolk** in the generation of CNFVs. The presence of egg yolk in the formula (FEPO) greatly modifies the profiles of aldehydes generated. The FEPO formula is well correlated with **long chain aldehydes** (C10 to C18) from phospholipids in the egg. The latter could, on the other hand, have an inhibitory role in the formation of short-chain oxidation aldehydes. Finally, the formula containing **egg yolk (FEPO) is strongly correlated with all of the Maillard compounds** identified in this study.

To clearly define the contribution of the various stages of cake production on lipid oxidation and the generation of volatile markers, we followed the progress of the lipid oxidation reaction by measuring oxidation markers (CNFV and conjugated dienes) in the dough (to test the effect of beating) and in cooked products (to test the effect of baking).

Figure 20 shows that lipid oxidation starts when the ingredients are whipped. The increase in the amount of conjugated dienes (specific absorbance values) in the dough is indeed significant for all the formulas and follows the same order as that determined by the analysis of the CNFV. After cooking the contents of dienes decrease significantly compared to the amounts found in dough but are always higher than those of native oils, which proves that oxidation also occurs during cooking. This final decrease may be due to the transformation of hydroperoxides into final products of LO such as volatile markers. These results are confirmed by a formula using pure linoleic acid (WELA) as fat, which makes it possible to amplify the oxidation effects during the various stages (polyunsaturated precursor more reactive than triglycerides).

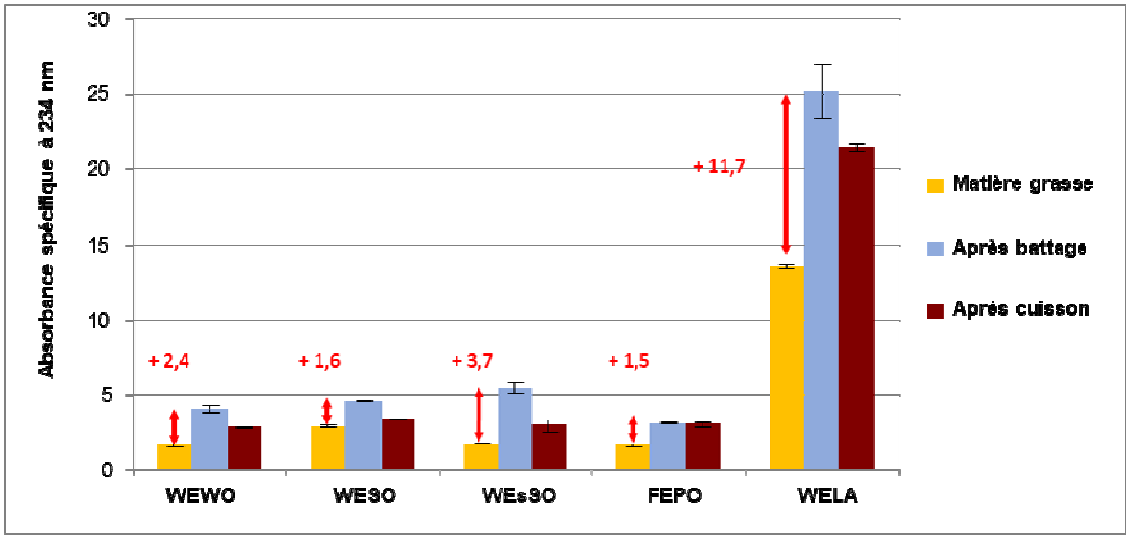


Figure 20: Specific absorption of conjugated dienes measured on pure vegetable oils or fats extracted from dough and sponge cake formulas. FEPO: reference formula with egg yolk and palm oil. WEWO: formula without yellow and without palm oil; WESO: formula without yellow and with sunflower oil; WEsSO: formula without yellow and with stripped sunflower oil; WELA: formula based on pure linoleic acid and without yellow. Based on (ACL8).

In conclusion, **the preparation of the dough seems to be the crucial step for lipid oxidation**. During this stage, the threshing incorporates air and leads to a foam which has a large contact surface between the oxygen and the reagents which could promote LO. On the other hand, active enzymes such as lipoxygenase and lipase could intensify the reaction. During cooking, the high temperatures deactivate these enzymes while promoting the lipid self-oxidation pathways which nevertheless remain moderate.

Interactions between reaction pathways: the case of interactions between Maillard reaction and Lipid oxidation

The interactions between the Maillard reaction and lipid degradation have been studied mainly in simplified model systems *(Whitfield, 1992, Zamora & Hidalgo, 2005)* or in products of animal origin in order to identify the odor compounds (*Mottram, 1998; Bertrand, Machado-Maturana, Chevarin, Portanguen, Mercier, Tournayre, et al., 2011)*. Concerning cereal products, it has been shown that specific and odoractive products such as long chain alkylpyrazines can be formed following the reaction between aliphatic aldehydes from LO and pyrazines from MR, especially during wheat flour extrusion *(Bredie, Mottram, & Guy, 2002).*

I wanted to investigate if interactions between MR and LO can occur in a formulated cereal product such as sponge cake, in a context where the replacement of fat could significantly increase the amount of aliphatic aldehydes generated.

So I imagined during the **M2 internship of F. Hanaei** *(Mast9)*, a strategy based on the addition of specific precursors of the alkylpyrazine formation pathway according to the simplified scheme previously discussed *(fig. 17)* , i.e. aliphatic aldehydes and free amino acids to sponge cake formulas.

If the addition of aldehydes alone did not show any effect on the generation of alkylpyrazines regardless of the level of unsaturation and chain length studied, the addition of selected amino acid (leucine) has important effects *(fig. 21)*. First, it activates the Strecker's pathway with an intensification of the formation of 3-methylbutanal *(fig. 21A)*. This then allows the formation of pyrazines and therefore longer chain alkylpyrazines *(fig. 21B)*. This result shows that the concentration of free amino acids was the limiting factor of the Strecker degradation pathway and therefore of the pyrazine formation pathway.

Additional analyzes in GC-GC/ToF-MS carried out in collaboration with J.L. Berdagué of INRA at Theix, corroborate the previous results by identifying a significant number of pyrazines formed (65 compounds). A principal component analysis (PCA) shows that the formation of alkylpyrazines is correlated with the addition of leucine or leucine and pentanal, in synergy. This aldehyde is important for the generation of dimethylpentylpyrazine (2,6-DMPP) and other medium chain alkylpyrazines (C4, C6) (*Zamora & Hidalgo, 2005)*. However, all the pyrazines identified in the enriched formulas are just as present in the reference sponge cake but in a trace amount.

These results therefore suggest that the **interaction pathway between oxidation aldehydes and pyrazines** is not favored in complex products such as sponge cake, under standard process conditions (baking at 170 ° C / 25 min). Studies using other free amino acids and other oxidation products could be conducted to generalize this result. In addition, GC-O analyzes could allow to identify the most odorant alkylpyrazines formed.

This work has highlighted the **key role of leucine for the formation of 3-methylbutanal and pyrazines**. The perspectives of this study are the identification of the many other compounds formed by high resolution methods and the determination of their concentration in the products via quantitative analysis. This study shows the advantage of using GC-GC/ToF-MS for an exhaustive study of all CNFV, which would allow the identification of the trace compounds of interest (eg odoractive and toxic ones) on the one hand, and interesting clues for the identification of reaction patterns in food as was done during the Reactial project on a cheese matrix by *Bertrand, Meyer, Machado-Maturana, Berdague, & Kondjoyan (2015).*

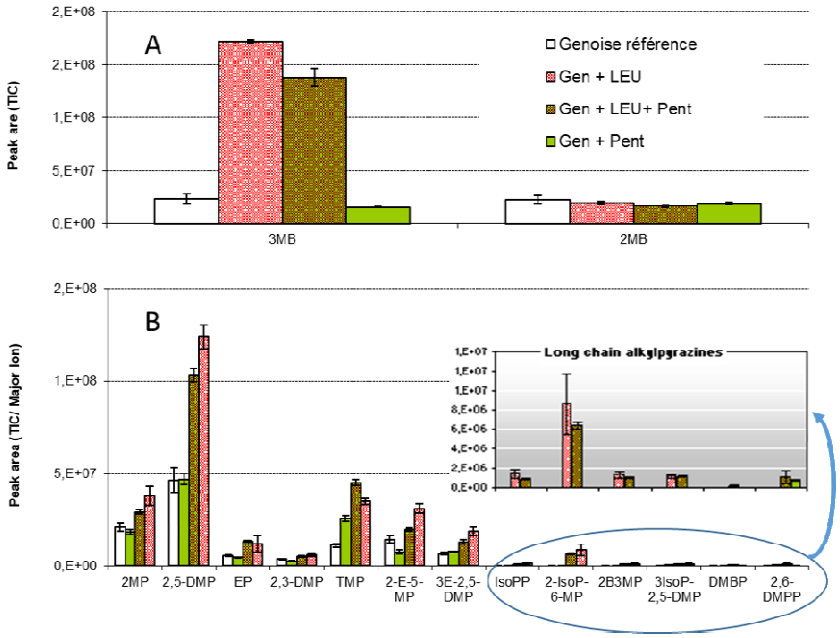


Figure 21: profile of Strecker's aldehydes (A) and of the main pyrazines (B) detected in 4 different sponge cake formulas. Génoise de reference: Reference sponge cake; Gen + Leu: sponge cake enriched in leucine, Gen + Pent: sponge cake enriched in pentanal; Gen + Leu + Pent: sponge cake enriched with leucine and pentanal. 3MB : 3-méthylbutanal; 2MB: 2-méthylbutanal ; 2MP : 2-méthylpyrazine ; 2,5-DMP : 2,5-diméthylpyrazine ; EP : éthylpyrazine ; 2,3-DMP : 2,3-diméthylpyrazine ; TMP : 2,3,5-triméthylpyrazine ; 2-E-5-MP : 2-éthyl,5-méthylpyrazine ; 3-E-2,5-DMP : 3-éthyl, 2,5-diméthylpyrazine ; IsoPP : Isopentylpyrazine ; 2-IsoP-6-MP : 2-Isopentyl, 6-méthylpyrazine ; 2B3MP : 2-butyl-3-méthylpyrazine ; 3IsoP-2,5-DMP : 3-Isopentyl, 2,5-diméthylpyrazine ; DMBP : diméthylbutylpyrazine ; 2,6-DMPP : 2,6-diméthyl-3-*n*-pentyl-pyrazine. Extraction HS-SPME (4g génoise ; Textr = 66 °C, tinc = 18 min, textr = 42 min) avec une fibre 50/30µm DVB/ Carboxen/ PDMS de 2cm. Analyse par GC/MS avec colonne DB5-MS de 30 m. Adapté d'après (*Mast9*).

Generation of furan in baked starch products: reactivity, occurrence and strategies for optimizing sensory and health quality

Furan is a newly formed IARC class 2B contaminant (possible carcinogen). The last EFSA assessment published in October 2017 highlights a health risk calculated using the margin of exposure (Margin of Exposure, MoE) for hepatotoxic and neoplastic effects (Knutsen, Alexander, Barregard, Bignami, Bruschweiler, Ceccatelli, et al., 2017).

Cereals and cereal products are the most important contributors to the baby, child and adolescent categories. Coffee is the main contributor to dietary exposure in adults and the elderly.

The formation of furan is induced by cooking processes via numerous reaction pathways such as the Maillard reaction, the breakdown of amino acids, sugars and vitamin C and even via the oxidation of lipids. There is therefore no specific precursor or reaction. Therefore, its formation is intimately linked to that of cooking aromas produced by the same routes. Understanding and preventing the formation of furan in processed foods has therefore become an important objective of the international scientific community.

In the period 2010-2017 I was therefore interested in the links between process and ingredients in the formation of this compound and this, not in canned products but in two widely consumed starchy products (target children's consumption): French fries for oven cooking during the **ANR – ALIA DOMINOVE** project (2010-2014) and cake-type products during the thesis project of **M. Cepeda Vazquez** (Th.4).

Generation of furan during domestic reheating of oven fried potatoes (ANR-ALIA Dominove project)

The originality of the Dominove Project was to focus on domestic (re)-heating because its impact on the sensory and nutritional qualities of food products is difficult to control. This is due to the consumers habits as well as the variability of household equipment (see summary of the project in chapter 5). The challenge of the project was to understand the process to better master the different dimensions of quality (optimization of the nutritional profile and maintenance of sensory quality).
We therefore carried out tests of reheating of oven-fried type products under conditions close to those encountered in domestic cooking but, here, perfectly controlled and reproducible thanks to a Dominove pilot oven specifically developed during the ANR project *(Cernela, Heyd, Keller , Bailleul, Maillard, Bonazzi, et al., 2015)*. We studied the influence of the temperature and the duration of reheating on the formation of furan when the other project partners studied the nutritional characteristics of the product, in particular the thermo-oxidative degradation of lipids and the possible presence of other newly formed compounds derived from this reaction.
One of the major results of the project was to show that in the reheating conditions covered by the project (nominal conditions and overheating of the worst-case type), the progress of the thermo-oxidative degradation reactions of the lipids (including oxidation of PUFAs) is very low (No or few markers of thermo-oxidation and degradation of PUFAs, no or very few newly formed compounds such as oxysterols, cyclic monomers, trans fatty acids were found). Most probably (and fortunately) the reheating conditions are not severe enough to induce oxidation. In addition, dissolved oxygen, a key reagent in the propagation phase of oxidation reactions, could be quickly limiting in these solid systems as shown in the case of model systems using the same oils *(Roman, Heyd, Broyart, Castillo, & Maillard, 2013)*. In the absence of criticality of the nutritional quality linked to the degradation of lipids, it would be logical to think that the predominant criterion for the optimization of this stage of the process is exclusively the sensory acceptability.
However, when we focus on the generation of furan, significant changes appear as a function of the time/temperature couple and the furan is detected in non-negligible concentrations.

Figure 22 shows the concentration of furan determined in the experimental plan implemented by Dominove. The two parameters (time and temperature) have a significant impact on the amount of furan generated and clearly the synergy between the two factors is very important and contributes positively to the formation of furan, with an amount multiplied by a factor of 60 between the lower and upper boundaries of the plan. It is interesting to note that the accumulation of furan seems to predominate over the possible diffusional loss (by evaporation) of furan which is a very volatile molecule. The formation of a crust impregnated with fat could here prevent the volatilization of furan. The significant increase in browning of these products with the time/temperature pair *(fig. 22)* and the results of limited degradation of the oils, therefore suggest that the furan does not result from lipid oxidation but from other reaction pathways such as Maillard reactions and/or caramelization, or even the degradation of vitamin C also present in potatoes.

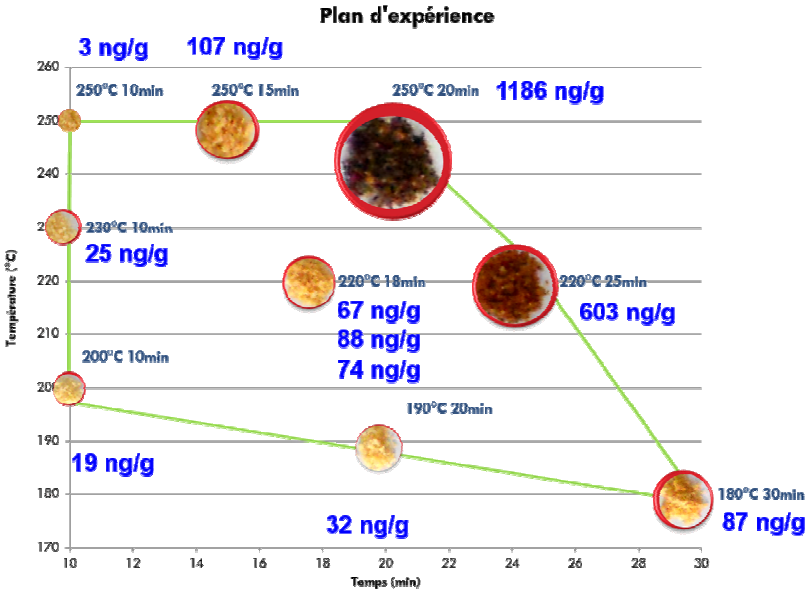


Figure 22: Furan concentration (ng/g of product on a dry basis) determined in "oven fries" cooked according to the experimental plan of the Dominove project. The lower boundary of the experiment plan (200°C/10 min) corresponds to the setting cooking conditions. Dosage by isotopic dilution and standard additions. HS extraction coupled with GC / MS analysis in SIM mode.

These results should not worry because the highest concentrations are found for high points corresponding to very cooked products, normally outside the acceptability zone of oven fries (1,186 ng/g at 250°C for 20min). It would be interesting to model these results to predict the concentration of furan throughout the study area using the modeling of response surfaces and correlate it with other measurements made by Dominove's partners. But these results arrived late (after the conclusion of the project) because of the difficulty of quantifying furan. This (as well as the confidentiality agreements) has delayed the exploitation and the complete valorisation of this part. These results could help in calculating the margins of exposure in high consumption scenarios (with overcooked consumption patterns) of products contributing to furan exposure. It will also be interesting to correlate these results with those concerning the accumulation of acrylamide, an undesirable newly formed compound (CNFI) typically found in fried potatoes and crisps.

Exploration of the levers offered by reactivity for quality design: Zoom on the case of furan and odor compounds in sponge cake

Prioritization of the reactive potential of the ingredients

As said before, sponge cake is a very interesting subject of study for its richness in reactive ingredients (sugars, fats, eggs) and the possibility of varying the cooking scales and mixtures of ingredients. Thus, we were able to have a fairly wide range of concentrations of markers while creating a space of sensory acceptable products.

In order to better understand the link between reactivity and quality, we have developed a simplified reaction scheme by adapting it to the ingredients present and the CNFVs monitored. Eleven CNFVs were selected as markers for the quality of cereal products. Among them, two have been quantified because they are considered paradigmatic with regard to the sanitary and sensory quality of the sponge cake: Furan (possible carcinogenic furan compound) as a marker of sanitary quality and furfural (odorous active furan compound contributing to the characteristic aroma of sponge cake) as an aroma marker. Certain reaction pathways are common to both compounds (Caramelization, Maillard reaction), some others are specific to furans (e.g. lipid oxidation, degradation of amino acids). The other volatile markers were chosen on the basis of our previous results on the sponge cake, in order to obtain additional information on the main reaction pathways occurring during cooking (ie caramelization, Maillard reaction and lipid oxidation), while being both flavor compounds of different chemical classes (aldehydes, pyrazines, etc.).
Thanks to a preliminary methodological step (cf. axis I), a systematic study was conducted on the ingredients of the sponge cake (fat, salt, sugar, egg products, *fig. 23*), as the first screening step formulation parameters.

The salient results of this study are reported here and are gathered in the article ACL 3 (Annex 1).

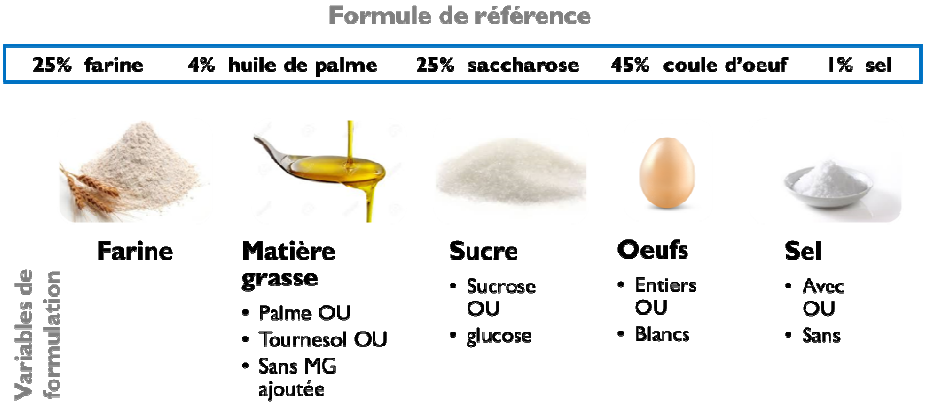


Figure 23: Reference formula and families of ingredients subject to change. According to the thesis of M. Cepeda Vazquez (Th4).

The results show that the type of sugar and the egg yolk are the classes of ingredients having the greatest impact on the generation of furan, furfural and aroma compounds in the sponge cake when the presence of fat, its level of unsaturation or the absence of endogenous antioxidants does not affect the furan content. This suggests that caramelization and the Maillard reaction are the predominant reaction pathways leading to the formation of furan in a cereal food formulated and baked in the oven, unlike the lipid oxidation which does take place in these products but which does not seem to lead to the formation of furan, as highlighted by the ACP analysis on the CNFVs derived from these formulas. In particular, if glucose is very important for the generation of furan and furfural, egg yolk is essential for the generation of aroma markers such as Strecker's aldehydes and pyrazines *(ACL3)*. These results confirm therefore those obtained by M. Maire and F. Hanaei.

Furthermore, the presence of salt does not affect the amount of furan generated and/or extracted, contrary to what has been reported in other studies on furan (salting out effect) or on the generation of other CNFs such as than acrylamide.

These studies also show that the generation of furan does take place in sponge cake-type products, whatever the formula but its concentration remains limited (between 3 and 12 ng/g) and much lower than that of furfural (between 0.3 and 9.2 µg / g, fig. 24).

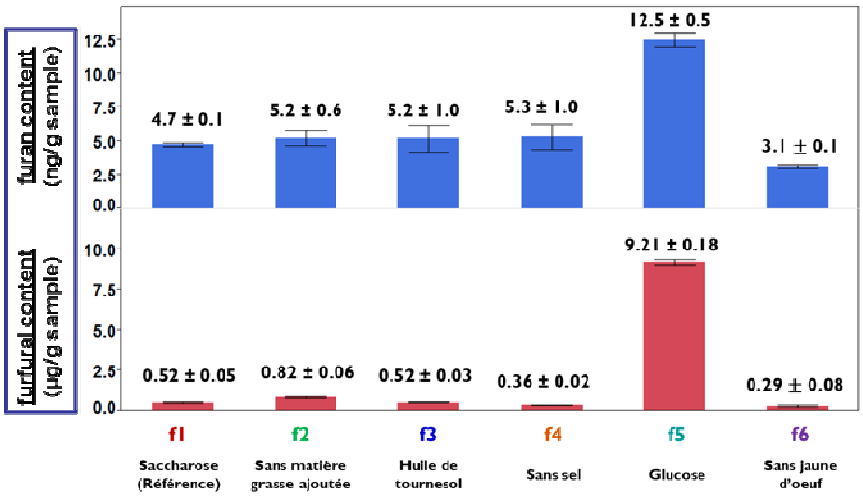


Figure 24: Furan and furfural content in 7 formulations obtained by varying reactive ingredients (baking at 170°C/30 min, sponge cakes of 20g). Adapted from ACL3.

Multivariate approach and multi-criteria optimization to understand the link between reactivity and quality

Following this first result, the formulation and the cooking conditions were jointly studied in order to produce changes in the central elements of reactivity: precursors and mass and heat transfers. An experiment plan combining a mixing and baking plan has been set up and **all the interactions between formula and process have been studied.** Within each selected ingredient (sugar, egg) we varied the nature of the ingredient while keeping constant the percentage in the overall formula (eg in the sugar class: 100% sucrose; 100% glucose and 50%/50% sucrose/glucose; in the egg class: 100% egg white, 100% whole egg and 50%/50% egg white/egg). Similarly, the limits of the process variables (time, cooking temperature) were chosen by meeting a double criterion: that the concentration of furan is quantifiable (lower boundary of the cooking level) and that the products are sensory acceptable (upper boundary of cooking level). The large amount of data obtained was processed by modeling response surfaces and PCA analysis to perform a multivariate analysis and then a multi-criteria optimization *(fig. 25)*, thanks to the collaboration with my colleague D. Blumenthal.

The salient results of this study are reported here and are gathered in the article ACL2 (annexe 1).

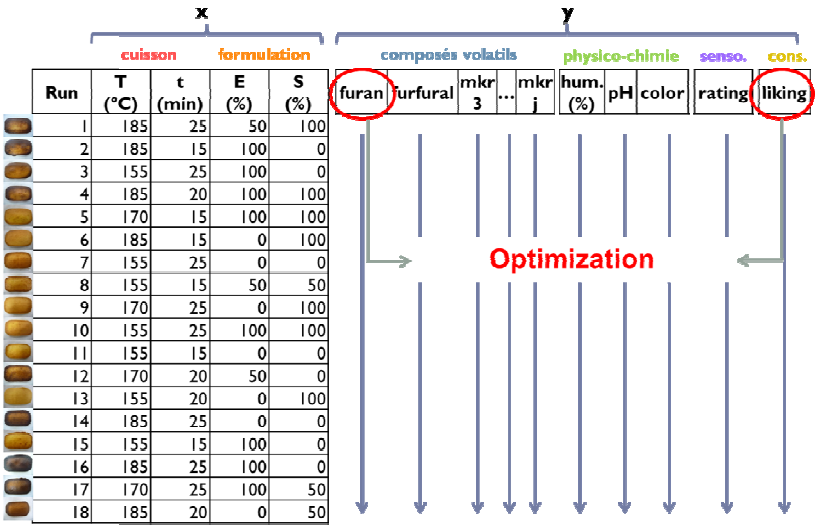


Figure 25: Optimal experiment plan for multivariate and multiresponse analysis, crossing formulation and cooking parameters. Four blocks of variables are measured; the quantities of volatile compounds (11 CNFV markers), the physicochemical properties (3 markers), the sensory notes and the hedonic notes. T: Cooking temperature; t: cooking time;

E: composition of the egg ingredient; S: composition of the sugar ingredient. According to the thesis of M. Cepeda Vazquez (Th4).

The models obtained are very significant and show that the content of these two furan compounds is affected in a very similar and significant way by the formulation, the cooking as well as their interactions (P> F: <0.0001 for the two variables). However, the content of furan remains low in most samples (of the order of ppb), while that of furfural can reach much higher levels (of the order of ppm) *(ACL2)*.

This suggests that the **predominant pathways** in the generation of furan are always those which are **common to furfural** (i.e. caramelization and/or the Maillard reaction), even when coupling the most extreme formulation and cooking conditions.

This also indicates that furfural can be used as a marker for the formation of furan in this type of product and reaction system, in particular for its easier analysis and its higher concentrations.

These studies have also made it possible to better understand the phenomena linked to reactivity. PCA analysis on all volatile markers *(fig. 26)* indeed shows that furan, furfural as well as 1-hydroxy-2-propanone are well correlated on the 2 main planes (95.8% of the information). When we consider the nature of sugar, it therefore appears that these compounds are formed predominantly via the same reaction path, that is to say the thermal degradation of glucose (via caramelization or the Maillard reaction). On the contrary, the formation of pyrazines, being well correlated with the presence of sucrose, requires hydrolysis of the sucrose (into fructose and glucose) prior to the Maillard reaction (via the degradation of Strecker).

These results therefore confirm the preliminary results obtained by SPME on sucrose, fructose and glucose formulas shown above: during cooking, the time and energy necessary for the hydrolysis of the non-reducing sugar favor, at the same time, the Strecker and Maillard pathways leading to the formation of pyrazines rather than 1 – hydroxy-2-propanone.

The link between the formation of Strecker's aldehydes and lipid oxidation products is visible because both classes are favored by the precursors present in egg yolk (free amino acids and PUFAs, respectively, *fig. 26*).

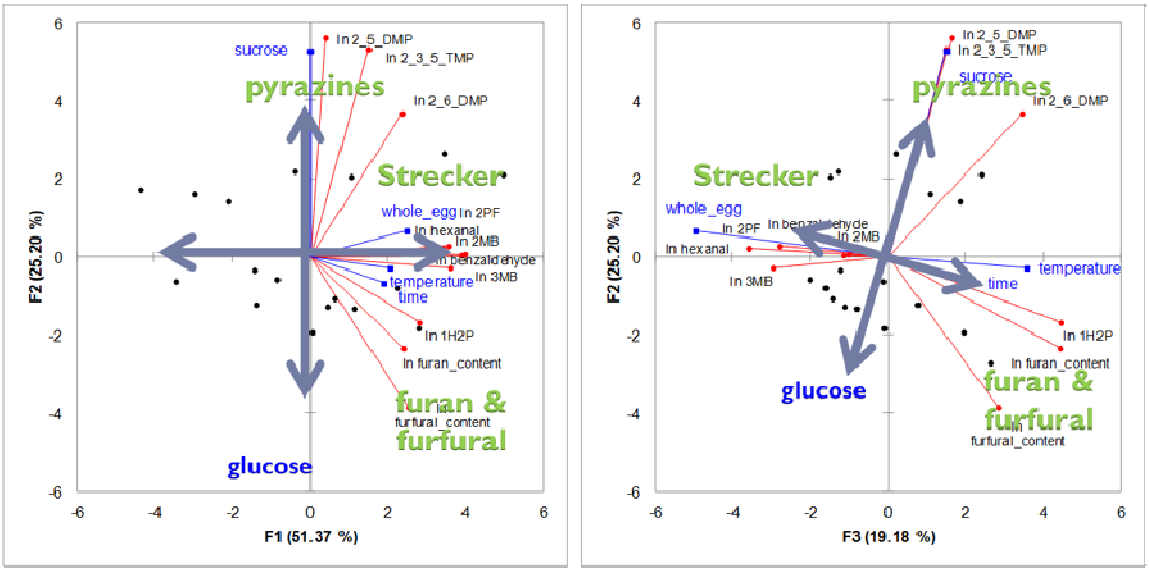


Figure 26: Principal Components Analysis of the quantitative and semi-quantitative responses of the sponge cake reaction markers according to the process and formulation variables studied by M. Cepeda (adapted from ACL3).

On the other hand, the strong correlation of 2-pentylfuran with hexanal (lipids degradation compounds) and with Strecker's aldehydes (produced via the degradation of amino acids) suggests that its generation in the sponge cake could take place via an interaction between the oxidation of lipids and amino groups, in addition to the oxidation of lipids simply, such as in the case of simplified models.

This work has also shown that the **synergy between formulation and cooking factors takes always place, regardless of the quality dimension taken into consideration** (ie generation of volatile compounds,

physicochemical properties, sensory properties and hedonic preference), but that the result on each of these dimensions (block of variables) remains different *(ACL3)*. **This "multidimensional" vision of quality therefore provides a more comprehensive and deep understanding of the impact of formulation and process** parameters on this type of product. A multi-block analysis with PLS methods integrating chemical and sensory knowledge could make it possible to better highlight the causal links between the different data blocks (eg which volatile markers could explain certain sensory descriptors and what could be the link of causality between sensory and physicochemical properties with hedonic notes).

As a last step, we have developed a **strategy to optimize the quality** of the sponge cake and have access to predictive models (profilers) based on the models previously obtained. Thanks to the use of the desirability function, it was possible to find **which levels of the formulation and process parameters allow at the same time the minimization of the amount of furan formed and the maximization of consumer preferences** *(fig. 27)*. The furfural content model was followed for information to see how it evolves relative to the levels of newly formed furan, to which it is intimately linked by the reaction pathways in the sponge cake, as previously shown.

Figure 27 shows that **furan mitigation and consumer liking** are not conflicting criteria. Products formulated with a low percentage of glucose (compared to sucrose) and cooked with fairly low time/temperature couples, result in a minimum amount of furan and an optimal preference. On the other hand, the presence of egg yolk can induce a certain amount of furan and at the same time increase consumer preference.

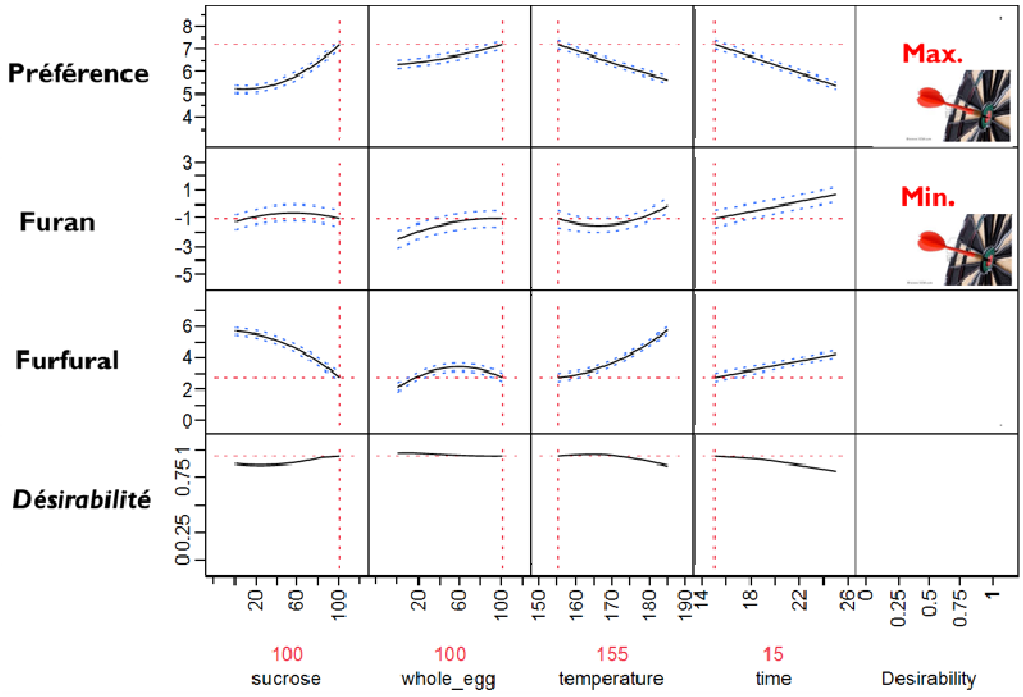


Figure 27: Prediction profilers with the desirability function: decrease in furan and consumer preference (adapted from ACL3).

However, the concentrations formed are always negligible compared to the aroma richness provided by this ingredient and it is possible to find a satisfactory compromise. Indeed, if we stop the “egg” factor at the value corresponding to hedonic optimization, the predicted furan content always remains very low, at levels close to the LOD. Indeed, the concentration of furan always remaining fairly low, it is possible to find areas which satisfy both the food safety criteria (furan levels) and sensory pleasure.

This work contributes to the development of food quality design strategies. During this work, we took into account the link between reactivity and quality and we focused on important aspects, such as the appearance of compounds linked to safety, sensory properties and consumer preference.

The scope of these studies is wide because this approach is adaptable to other products and of course to the needs of risk management. For example, the desirability function could be modified by moving the cursor to limits imposed by new recommendations while meeting the criteria of sensory pleasure. In addition, depending on the type of product, a new mapping of the relevant quality indicators could lead to the addition of new criteria to the desirability function (e.g. protective water activity levels vis-à-vis the microbiological risk, levels of certain nutritional markers, preserved functional properties).

This would help define how different aspects of quality relate to each other, or how variables of different dimensions of quality are correlated for a given product area.

To conclude, it is important to emphasize that optimization strategies are indeed strictly linked to the couple ingredients/process. We were able to see in the case of oven-fries that the impregnation of crust oil could prevent the volatilization of the furan and thus favor its accumulation in the ready-to-eat product. However, although the levels detected are much higher than for sponge cake, it would seem that lipid oxidation is not involved in the generation of this compound, as in the case of sponge cake.

Highlights of Axis II

1. In the case of alveolar cereal products, **lipid oxidation occurs very early** during the dough preparation stage (beating with incorporation of air) and to a lesser extent during the cooking process.
2. The **endogenous antioxidants** of vegetable oil protect formulas with high PUFA content from oxidation.
3. The compounds present in **egg yolk** protect PUFAs from oxidation, while generating a large class of Maillard CNFVs.
4. The presence of **reducing sugars** such as fructose and glucose promotes the formation of furanic compounds and acetic acid and, at the same time, seems to disadvantage the formation of pyrazines, unlike sucrose.
5. **Leucine is the factor limiting the formation of 3MB** Strecker's aldehyde and, in turn, alkylpyrazines.
6. **The interactions** between Maillard reactions and lipid oxidation seem limited because the alkylpyrazines remain in a trace state under the reference formulation and cooking conditions.
7. For the first time the **formation of furan has been studied jointly with that of aroma compounds** in a food product and its formation is strongly correlated with that of furfural in all the formulations studied.
8. The **glucose degradation pathways** (MR and/or C) seem to be the predominant reaction pathways leading to the formation of furan unlike the oxidation of lipids.
9. Numerous **interactions between formulation variables and cooking conditions** are highlighted for the generation of CNFVs and the quality determinants in sponge cake.
10. A multi-criteria optimization has made it possible to propose a **strategy for minimizing furan** and maximizing hedonic appreciation in the case of sponge cake.

Professional development and promotion aspects

11. I have **developed expertise on the interactions between formulation and process**, in particular on cereal products.
12. I **designed the PhD thesis subject of M. Cepeda Vazquez** (th3) and I took the main responsibility during her supervision (doctoral student with high potential).
13. We valorized the main results by **4 ACLs published in Food Chemistry**.

Advantages and limitations of reaction studies conducted in real foods

With the works shown in this section, we studied the formation of CNFVs related to quality and oriented the work towards a methodological and application purpose for a reasoned construction of quality.

At the same time, in order to understand the links between quality and reactivity, and as much as possible for a complex product such as sponge cake, we also tried **to explore and formalize an apparent reaction scheme by a deductive process** and we integrated hypotheses from our previous work where we converged knowledge on volatile compounds of interest and knowledge on reactions.

This deductive approach based on a real product has a definite advantage over the numerous works carried out in recent decades in model systems. These systems are generally close ones and consist of simple liquid mixtures where the precursors enjoy significant mobility. In these systems, the medium is continuous and the reactions can occur homogeneously.

In a product like sponge cake, on the contrary, we bring into play a significant diversity of reactants provided by the ingredients and, at the same time, spatial and temporal differences in their availability and mobility. Indeed, heat and mass transfers evolve during cooking and this, in turn, has an impact on the induction and evolution of chemical reactions. As a result, **the reactivity in very simple or simplified models can sometimes differ from that in real food.** For example, it has been shown that the amount of furfural formed in the case of model solutions containing glucose *(Kocadagli & Gokmen, 2016)* is not affected, when it increases significantly in the case of sponge cake and others products such as cookies *(ACL15).*

While simple models cannot reproduce the reaction and the steric and dynamic complexity of a real food, studies in real products cannot answer all of the questions about the reactivity of a given food product either.

For example, in the case of a real sponge cake, it will be impossible to go very far in understanding the reaction kinetics, or even to verify the hypotheses on the reaction pathways occurring during heat treatment, taking into account the impossibility of following and/or mastering the wide range of precursors/cofactors present in the ingredients and potential intermediates which will be formed.

This underlines the importance of carrying out additional research into **realistic food models** and under controlled processing conditions.

This complementary approach will be developed in the third and last section of this chapter.

Axis III : Understanding of reaction mechanisms and kinetics in products during cooking Mes questions guides

- How to follow the reaction kinetics in cooked products in a representative and informative way?
- How to overcome the complexity of the ingredients and identify the main reaction mechanisms?
- Is it possible to predict/model the kinetics and therefore the generation of CNFV of interest?

In the previous section, we have shown that CNFVs develop at different times during food making, depending on their reaction origin. Thus, while certain lipid oxidation products are formed mainly during the whipping step, pyrazines and Strecker's aldehydes are formed quite early during baking whereas furanic compounds accumulate at the end of cooking.
To have a better understanding of the thermal reactivity in a solid cereal product, it is interesting to **follow kinetically the formation of these CNFVs,** that is to say over time and as a function not of a nominal baking temperature (the oven set point) but by coupling it to the most relevant physical variables, that is to say measured on the product in transformation throughout cooking. We have also shown the interest of having quantitative methods of assay to be able to go further in the reaction hypotheses on the more active paths on the one hand, but also to access to robust modeling and optimization methodologies.

In this last section, I will therefore summarize the work that has focused on the kinetic monitoring of these reactions as a function of physical transformations due to baking, in particular thanks to **two complementary strategies: first in real products, during the thesis by S. Fehaili** *(Th1)* **and the ANR Reactial project and, then, on model products during two successive doctoral theses: those of J. Bousquières** *(Th3)* **and J. Lee** *(Th5)***.**

Development of a reaction engineering approach to monitor the reactivity of the sponge cake

Understanding of the sponge cake system during cooking

During baking, heat transfer occurs through all modes, namely conduction, convection and radiation. Under these conditions, the structure of the sponge cake changes throughout cooking from a liquid and viscoelastic foam to a solid foam made up of two compartments: (1) a moist alveolar crumb -obtained following the starch gelatinization and egg protein gelation- and (2) a brown crust -obtained by drying the surface of the product. The exchanges are done in an open system. The air bubbles incorporated during whipping expands, the water vapor goes from the heart to the surface and from the surface to the over atmosphere trough chimneys formed by open *alveoli*. The mobility of the reagents may be limited due firstly to the viscosity of the dough, and secondly to the solidification of the honeycomb system during baking.

During the cooking of this product, the core and surface temperatures rise rapidly during a first stage (heating), then slowly reach a plateau (evaporative state) and finally, while the humid heart remains around 100°C, the surface temperature tends towards that of the oven setting (e.g. 170°C). High surface temperature and high drying speed are responsible for crust formation and can accelerate thermal reactions.

The reaction engineering methodology applied to a complex solid product (sponge cake)

Characterize the transformations of such an evolutionary system during baking was my first objective. I applied a reaction engineering approach in order to acquire synchronous kinetic and thermal data during the ANR Reactial project (see summary in chapter 4), *(fig. 28)*.

This choice led us to a reflection on the way of apprehending the reactions starting from the experimental information accessible thanks to the collaboration with my colleagues of process engineering (C. Bonazzi, M.

Courel) and Xuan Meyer of the INP-ENSIACET from Toulouse. The reaction systems studied can be described as complex networks of chemical reactions, for which only a part of the phenomena is observable *(ACT4)*. A major stake of the thesis of S. Fehaili *(Th1)*, was therefore to simplify the systems studied in order to extract a simplified reaction scheme, but identifiable and capable of giving an adequate representation of the systems.

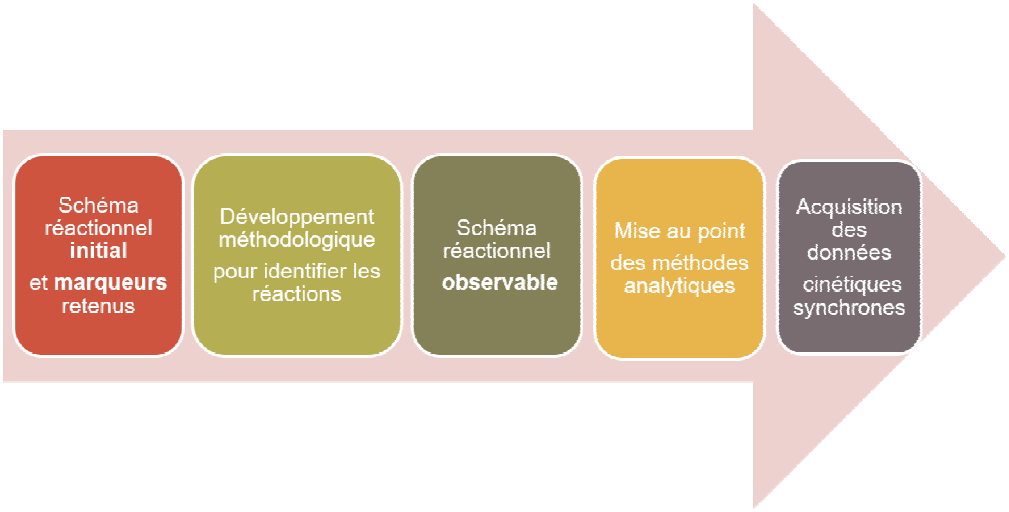
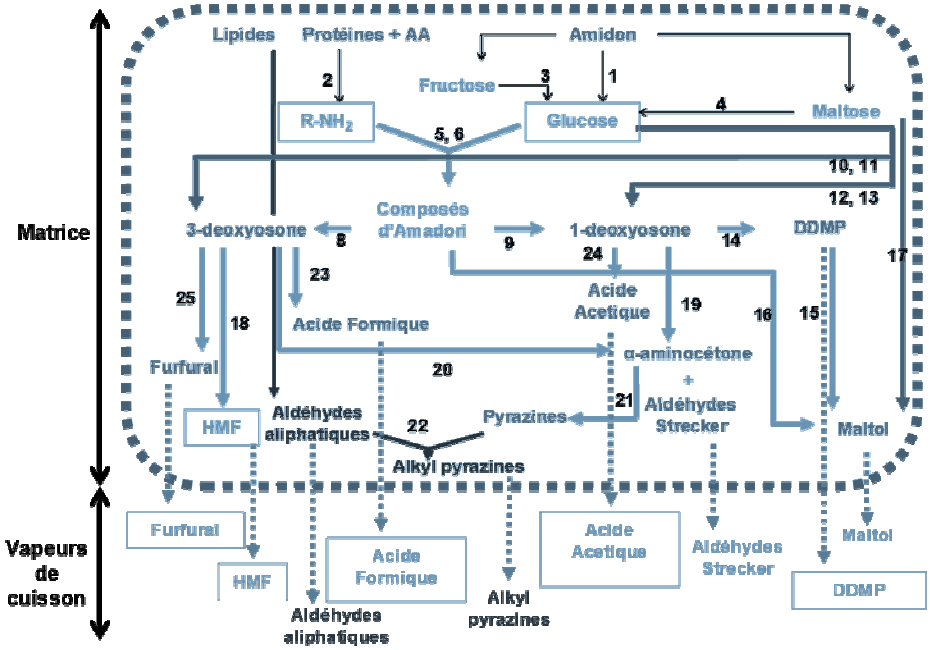


Figure 28: Stages of the reaction engineering methodology implemented as part of the thesis of S. Fehaili (Th1), during the Reactial project.

From a very complete initial reaction scheme written "*a priori*" on the basis of bibliographic knowledge and my previous work, we built a stoichiometric matrix comprising 23 constituents and 25 reactions *(fig. 29)*. Then, a simplification of this scheme was necessary because of the limited number of experimentally measurable markers (only 7) and the interdependence of certain reactions.

This gave rise to an observable scheme (*i.e.* a scheme whose speeds of the resulting reactions will be identifiable from the monitoring of the concentrations of the different markers). It was very simple and made of six balance reactions (i.e. resulting from the combination of several elementary reactions) belonging only to the families of Maillard reactions and caramelization.



N°	Code	Nom	Réaction	Réaction avec formules
1	AMID	Hydrolyse de l'Amidon	Amidon + (x + y) H_2O → x glucose + y fructose	$(C_6H_{10}O_5)_n$ + (x + y) H_2O → x $C_6H_{12}O_6$ + y $C_6H_{12}O_6$
2	PROT	Hydrolyse des protéines	Proteines + pH_2O → p$R\text{-}NH_2$	-
3	GLUC	Isomerisation du glucose	Glucose ⇄ fructose	$C_6H_{12}O_6$ ⇄ $C_6H_{12}O_6$
4	MALT	Hydrolyse du maltose	Maltose + H_2O → 2 glucose	$C_{12}H_{22}O_{11}$ + H_2O → 2 $C_6H_{12}O_6$
5	AMAD1G	Formation du composé d'Amadori à partir du glucose étape précoce de la réaction de Lys bird	Glucose + $R\text{-}NH_2$ ⇄ Amadori + H_2O	$C_6H_{12}O_6$ + $R\text{-}NH_2$ ⇄ $R\text{-}NC_6H_{11}O_5$ + H_2O
6	AMAD1F	Formation du composé d'Amadori à partir du fructose étape précoce de la réaction de Lys bird	Fructose + $R\text{-}NH_2$ ⇄ Amadori + H_2O	$C_6H_{12}O_6$ + $R\text{-}NH_2$ ⇄ $R\text{-}NC_6H_{11}O_5$ + H_2O
7	AMAD2	Formation du composé d'Amadori à partir du Maltose étape précoce de la réaction de Lys bird	Maltose + $R\text{-}NH_2$ ⇄ Amadori + H_2O	$C_{12}H_{22}O_{11}$ + $R\text{-}NH_2$ ⇄ $R\text{-}NC_{12}H_{21}O_{10}$ + H_2O
8	DEOS1 2	Formation 3 deoxyosone	Amadori → 3 deoxyosone + $R\text{-}NH_2$	$R\text{-}NC_6H_{11}O_5$ → $C_6H_8O_4$ + $R\text{-}NH_2$
9	DEOS2 3	Formation 1-deoxyosone	Amadori → 1-deoxyosone + $R\text{-}NH_2$	$R\text{-}NC_6H_{11}O_5$ → $C_6H_8O_4$ + $R\text{-}NH_2$
10	CARA1 2G	Formation 3 deoxyosone par caramélisation du glucose	Glucose → 3-deoxyosone + H_2O	$C_6H_{12}O_6$ → $C_6H_8O_4$ + H_2O
11	CARA1 2F	Formation 3 deoxyosone par caramélisation du fructose	Fructose → 3 deoxyosone + H_2O	$C_6H_{12}O_6$ → $C_6H_8O_4$ + H_2O
12	CARA2 3G	Formation 1 deoxyosone par caramélisation du glucose	Glucose → 1 deoxyosone + H_2O	$C_6H_{12}O_6$ → $C_6H_8O_4$ + H_2O
13	CARA2 3F	Formation 1 deoxyosone par caramélisation du fructose	Glucose → 1 deoxyosone + H_2O	$C_6H_{12}O_6$ → $C_6H_8O_4$ + H_2O
14	PYRA	Formation de DDMP à partir de 1-deoxyosone	1 deoxyosone → 2,3 dihydro 3,5 dihydroxyl methyl 4(H) pyran 4 one + H_2O	$C_6H_8O_4$ → $C_6H_8O_4$ + H_2O
15	MALTOL 1	Formation du maltol à partir de la DDMP	2,3 dihydro 3,5 dihydroxyl methyl 4(H) pyran 4 one → maltol + H_2O	$C_6H_8O_4$ → $C_6H_6O_3$ + H_2O
16	MALTOL 2	Formation du maltol à partir d'Amadori	Amadori → maltol + 2 H_2O + $R\text{-}NH_2$	$R\text{-}NC_6H_{11}O_5$ + $C_6H_6O_3$ + 2 H_2O + RNH_2
17	MALTOL_3	Formation du maltol à partir du maltose	Maltose → maltol + glucose	$C_{12}H_{22}O_{11}$ → $C_6H_6O_3$ + $C_6H_{12}O_6$ + 2 H_2O
18	HMF	Formation de HMF à partir du 3-deoxyosone	3-deoxyosone → HMF + 2 H_2O	$C_6H_8O_4$ → $C_6H_6O_3$ + 2 H_2O
19	PyH 1	Formation Aldehydes de Strecker à partir d.. 1 deoxyosone	1-deoxyosone + R-NH2 → aminocétone + Aldehyde de Strecker + CO_2	$C_6O_4H_8RNH_2$ + $C_6H_{10}O_5$ → $C_6H_{11}O_4R$ + RCHO + CO_2
20	PyH 2	Formation Aldehydes de Strecker à partir d.. 3-deoxyosone	3-deoxyosone + R-NH2 → aminocétone + Aldehyde de Strecker + CO_2	$C_6O_4H_8RNH_2$ + $C_6H_{10}O_5$ → $C_6H_{11}O_4R$ + RCHO + CO_2
21	PyH_3	Formation de pyrazines à partir de deux aminocétones	2R-CO-CHNH2-R_2 → PyH + 2 H_2O	2R-CO-CHNH2-R_2 → PyH + 2 H_2O
22	PYR	Formation de alkylpyrazine à partir d'un aldéhyde (oxydation des lipides) et d'une pyrazine	PyH + RCHO → RPy + H_2O	PyH + RCHO → RPy + H_2O
23	FORM	Formation de l'acide formique à partir du 3 deoxyosone	3 deoxyosone + H_2O → Acide Formique + 2-deoxyribose	$C_6H_8O_4$ + H_2O → CH_2O_2 + $C_5O_4H_8$
24	ACET	Formation de l'acide acetique à partir du 1 deoxyosone	1 deoxyosone + H_2O → Acide Acetique + Hydrose	$C_6H_8O_4$ + H_2O → $C_2O_2H_4$ + $C_4O_3H_4$
25	FUR	Formation du furfural à partir du 3-deoxyosone	3-deoxyosone → Furfural + CH_2O + $2H_2O$	$C_6H_8O_4$ → $C_5H_4O_2$ + CH_2O + $2H_2O$

Figure 29: Initial reaction scheme and its relative reaction matrix according to the thesis of S. Fehaili (Th1).

The kinetics of these thermal reactions have been studied at different cooking temperatures (140, 170 and 200°C) by following the **7 quantifiable reaction markers**. Markers were **followed both in the matrix** by

quantitative assays (glucose, reactive amino groups, HMF) and **in the baking vapors** (furfural, DDMP, acetic acid, formic acid, HMF) by the semi-quantitative methods that I discussed in *axis I*. These markers were measured synchronously to the physical characteristics (air humidity, air, surface and core temperatures, humidity and pH in the product) thanks to the **Reactial oven** developed during this project.

Figure 30 shows an **example of the results obtained on the degradation of the precursors** (glucose and free amino-groups) and the **concomitant formation of 3 CNFVs**. It is not surprising to see that the rates of precursor degradation and product formation strongly depend on the baking temperatures.

Glucose is present in large excess *vis-à-vis* the free amino groups (100 times more important, because it is added as an ingredient at 25% in the formula). Its degradation at 140 °C is not significant since it is probably included in the confidence interval of the measurements. On the contrary, the degradation of R-NH_2 is already observable at 140 °C. Glucose seems to be consumed in general always in a higher quantity than the R-NH_2 functions; the higher the temperature the higher this difference is large (from 4 to 27 times greater).

Two hypotheses could help explain such a difference in the rates of consumption of precursors. First, at higher temperatures glucose can be consumed by reactions other than Maillard, such as fructose isomerization and caramelization, and second, free amino groups could be regenerated in reactions downstream of the Amadori rearrangement. The acidification of the matrices during baking is evident and this could also promote caramelization and isomerization (decrease of 2 pH points at the end of cooking at 200 °C).

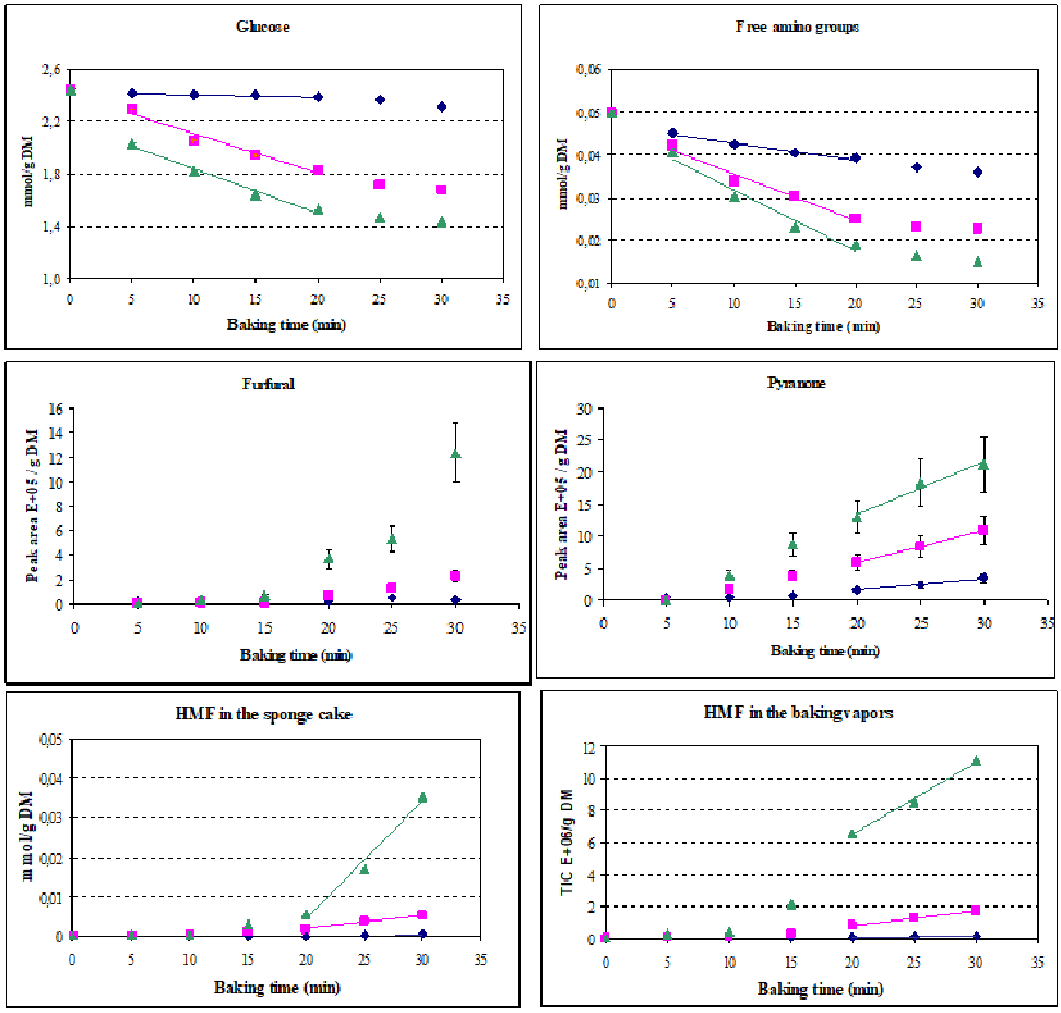


Figure 30: Degradation of precursors (glucose, free amino groups) in the sponge cake matrix and concomitant generation of certain volatile markers followed in cooking vapors with the Reactial oven. The HMF is monitored in the two compartments. Kinetics performed at 3 different cooking temperatures: 140°C (◆), 170°C (■) and 200°C (▲). Adapted from S. Fehaili's PhD thesis (*Th1*).

On the other hand, the generation of HMF and pyranone (DDMP) is all the faster the higher the baking temperature *(fig. 30).*

At 140°C, the HMF (issued from the 1,2-enolization pathway) is detected at trace level, while DDMP (from the 2,3-enolization pathway) forms in higher amounts. It is interesting to note that at 200°C this ratio is reversed (faster formation of HMF). This could suggest the prevalence of the 2,3-enolization pathway at 140°C (in correspondence with the higher humidity levels in the product) and a prevalence of the 1,2-enolization pathway at 200°C (in correspondence with the lower humidity in the product which dries faster).

Figure 31 shows a model adjusted to the experimental points of HMF generation. This model uses the temperatures measured on the surface of the product during cooking and applies a zero order kinetics (dP = k*dt) with the reaction rate defined as a temperature function, according to Arrhenius. This choice emphasizes the fact that the glucose precursor is in very large excess (G ➔ HMF). Two parameters (k_0 and *E*a) are identified for the kinetics obtained at 4 different cooking conditions (140°C, 170°C, 170°C $_{\text{low fan speed}}$ 200°C). The apparent kinetic parameters are $k_0 = 3.7 \times 10^{15}$ mmol/min and *E*a = 153 kJ/mol.

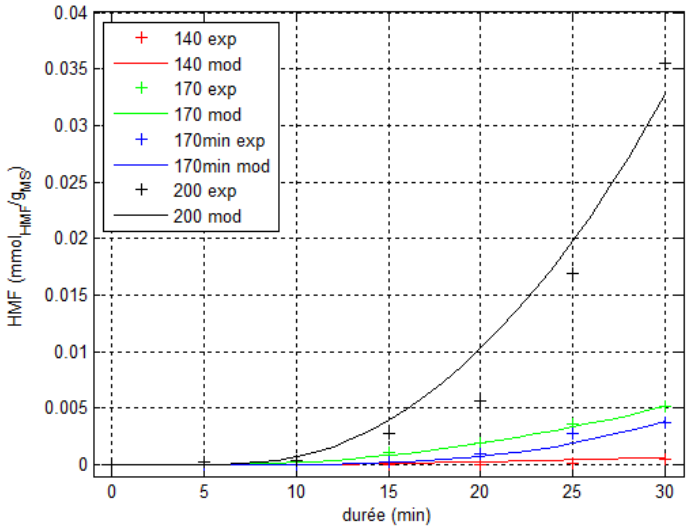


Figure 31: Tentative model of HMF production using zero order kinetics. Calculations were made by my colleague Bertrand Heyd under Matlab.

With this work, we **laid the methodological bases for a new approach in several steps** (writing a theoretical diagram, identification of an identifiable diagram, acquisition of targeted data, modeling), based on reaction engineering to identify and model the Maillard and Caramelization thermal reactions in a real product. The results have shown the interest of such a methodological tool, that is to say the possibility of having access to kinetic measurements under real transformation conditions. For the first time we were interested in quantitative methods of assaying volatile markers, because for kinetic modeling it is essential to have access to concentrations of markers. However, the very large number of precursors present in the formula and the limited number of markers and quantifiable intermediaries at the time allowed the formalization of a far too simple reaction scheme (the observable scheme) which did not allow the Maillard pathways to be separated from the caramelization pathways, because we did not have data on discriminating precursors or intermediates.

To overcome these limitations, we worked on two planes: 1) greatly simplify the composition while preserving a complex (porous) structure and (2) increase the number of markers dosed.

Study of reactivity in a model product with controlled composition and structure

Development of a model product mimetic of a sponge cake

In order to deepen the understanding of the reaction mechanisms and kinetics previously discussed, we have set up an original approach to **study reactivity in a solid medium that is physically representative and chemically controlled**.

To do this, we set up a major collaboration (2 master internships, J. Bousquières' PhD thesis) within the two research teams SP2 and Calipro of the UMR Genial (expertise in biophysics, biochemistry and thermal physics). This collaboration resulted in the development of a model product which, being subjected to the same thermomechanical manufacturing steps as the sponge cake, is capable of developing the same structural characteristics of a true sponge cake without developing its reactions, since it lacks any reactive ingredient. *(fig. 32).*

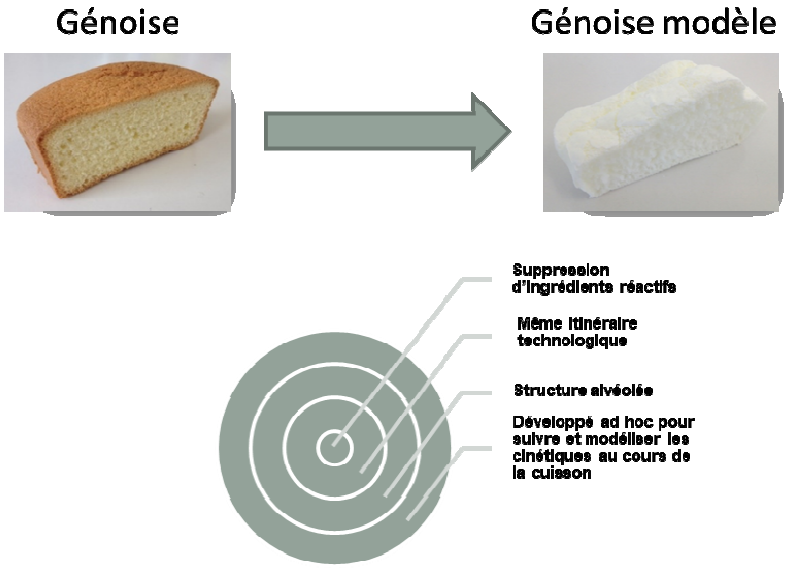


Figure 32: Strategy implemented for the development of the model sponge cake.

The study of the functionalities provided by each ingredient at each stage of the manufacturing process allowed the complete replacement of the reactive ingredients (egg, sugar and flour proteins) by starch and two cellulose derivatives. We have thus shown that this product is completely inert to Maillard and caramelization reactions and does not produce, for example, furanic compounds *(fig. 33).*

This "inert" sponge cake served us for targeted reactivity studies in which we introduced a known quantity of precursors chosen to initiate thermal reactions in a controlled manner.

The G model was therefore formulated with the addition of glucose (model where only caramelization can take place) and the **G + L model** was obtained by adding known quantities of glucose and leucine (model where the Maillard and caramelization reactions can take place). These two precursors were chosen following the results obtained in the previous studies presented in *axis II.*

These two "enriched" formulas were then subjected to baking with the Reactial oven with kinetic monitoring of the markers as previously presented in *axis I* with the objective of comparing the reactivity markers obtained with or without leucine and of measuring their kinetic velocities *(fig. 34).*

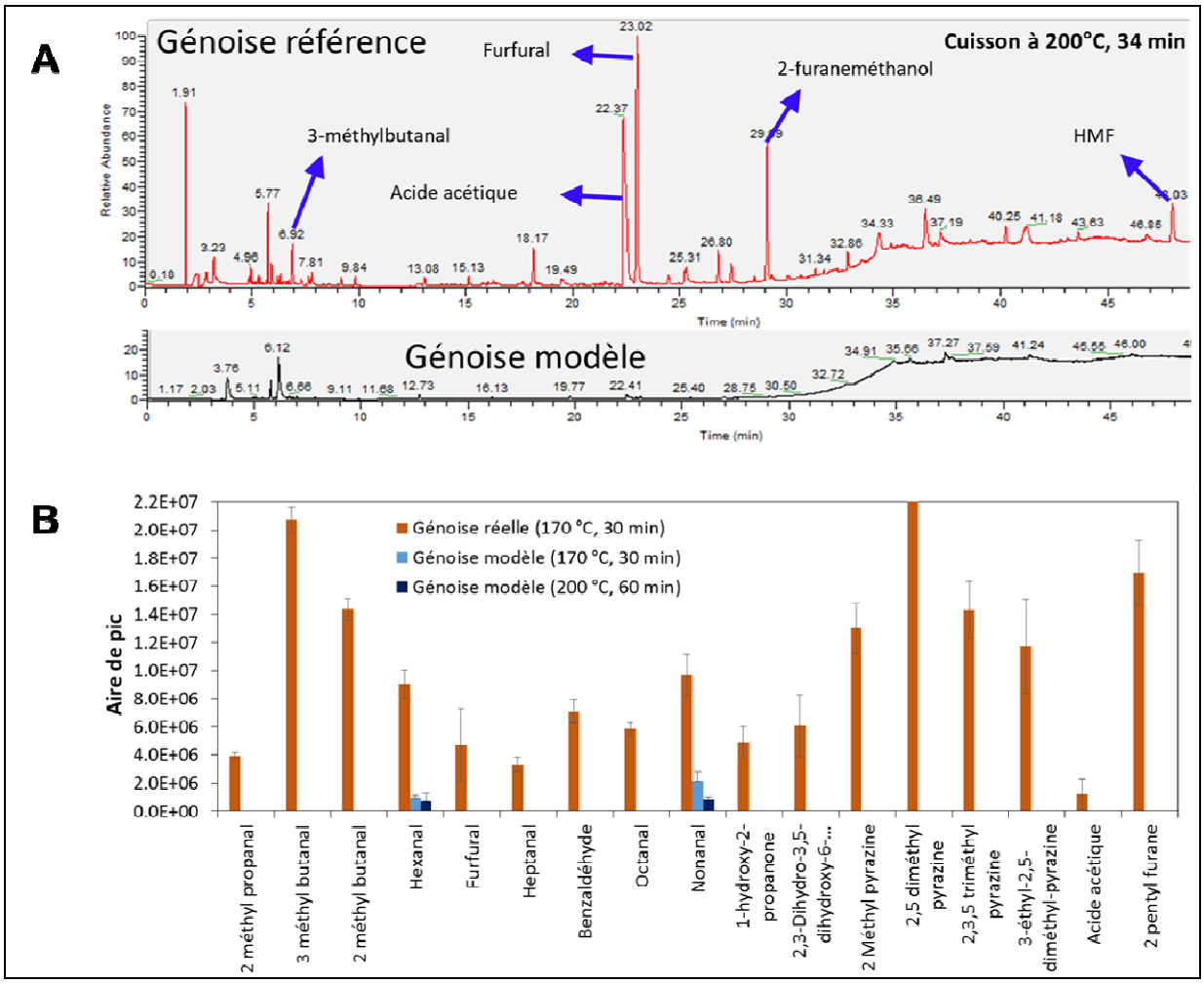


Figure 33: GC-MS Profiles of CNFV generated by the reference and the model sponge cakes. The sampling was carried out by on-line TD sampling of cooking vapors (A) and by HS-SPME on the final products. According to the PhD thesis of J. Bousquières (Th3).

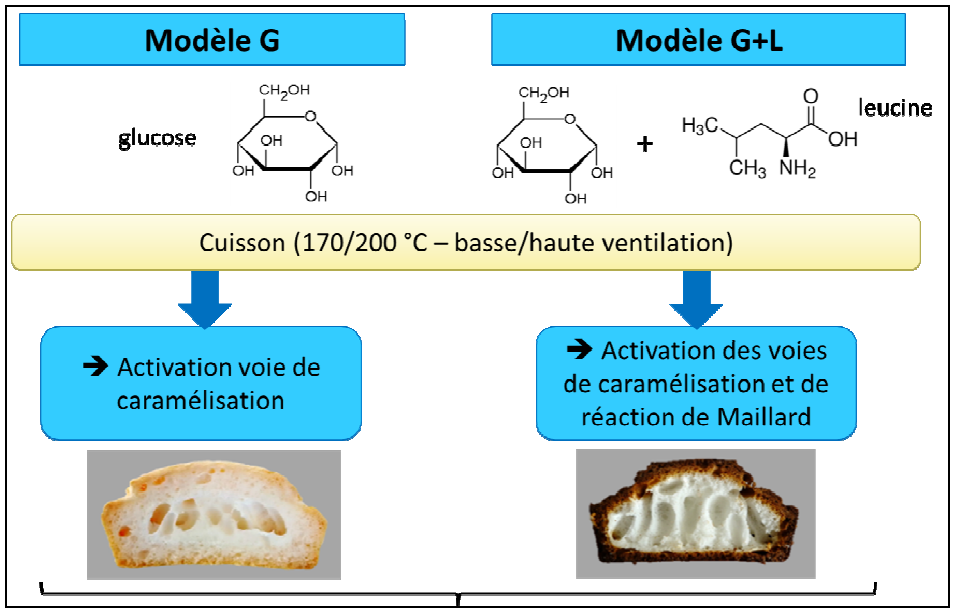


Figure 34: Strategy implemented for the activation of the Maillard reaction and caramelization pathways within the model product. Model G: model sponge cake enriched in glucose; Model G + L: model sponge cake enriched with glucose and leucine. Adapted from the PhD thesis of J. Bousquières (Th3).

Example of kinetic monitoring of furan and furfural in the model products

By relying on the involvement of an exceptional FIPDes master student (R. Srivastava, Mast13) **I had the idea of setting up a collaboration between doctoral students** in order to kinetically monitor furan and furfural by the method developed by M. Cepeda Vazquez in the models G and G + L studied by J. Bousquières.

When the precursors are introduced into the model product, browning develops during cooking, as evidence of the initiation of thermal reactions. This browning is much more important for the G+L model *(fig. 34)*. This induced reactivity generates significant levels of furanic compounds (up to 17.61 ng/$g_{dry\ basis}$ for furan and 38.99 µg/$g_{dry\ basis}$ for furfural). However, furfural is found in quantities much higher than those of furan (ppm versus ppb). For the two compounds, the concentrations increase with the cooking time and are influenced differently by the nature of the precursors *(ACL4).*

Indeed, furfural was formed at much higher concentrations in the presence of leucine and glucose (model G+L) than in the model containing only glucose (G). We deduce that the **difference in concentration of furan compounds in the model cakes is only due to the presence of leucine, the thermal conditions being strictly identical between the models G and G + L.** Interestingly, the higher the level of browning, the higher the concentrations of furfural, but this is not the case for furan (G and G+L have very different levels of browning for comparable levels of furan). This therefore suggests that **browning is not well correlated with the concentration of furan.**

It should be noted that a real sponge cake subjected to the same treatment conditions (baking at 170°C/34 min in the same oven) contains a similar rate of furan but a furfural concentration 15 times lower than that found in the G + model L. This thus shows the crucial role of ingredients as a source of reagents.

By having a very simple reaction system (only two precursors) we were able to write a reaction diagram with 6 reactions *(fig. 35).*

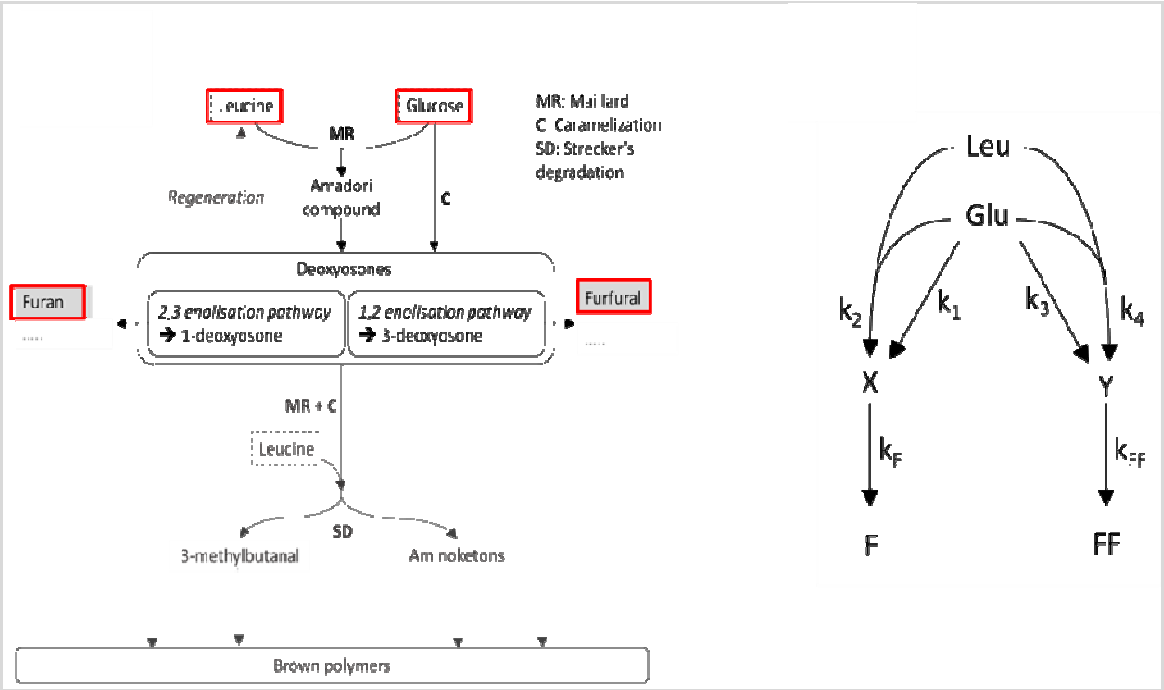


Figure 35: Simplified reaction scheme with the Maillard reaction (MR), caramelization (C) and Strecker (SD) degradation pathways occurring in model sponge cakes containing glucose and leucine. This diagram is translated into an apparent diagram with 6 reactions: the consumption of the precursors, leucine (Leu) and glucose (Glu), the production of furan (F) and furfural (FF) by two fictitious intermediaries (X, Y). The kinetic speed constants (k) associated with the 6 reactions are also presented: $k_1 = 8.3 \cdot 10^{-7}$ s^{-1}; $k_2 = 1.7 \cdot 10^{-3}$ g_{DM} $mol^{-1}.s^{-1}$; $k_3 = 1.2 \cdot 10^{-5}$ s^{-1}; $k_4 = 2.1 \cdot 10^{-1}$ g_{DM} $mol^{-1}s^{-1}$; $k_F = 7.7 \cdot 10^{-6}$ s^{-1}; $k^{FF} = 3.4 \cdot 10^{-4}$ s^{-1}. Following *(ACL4).*

Kinetic modeling was then carried out to identify the apparent kinetic speed constants for each of the 6 reactions, in collaboration with my colleague S. Roux. The values identified are used to describe the trend

illustrated by the kinetic curves *(fig. 36).* First of all, **furfural forms faster than furan** (k3 vs k1; k4 vs k2 and kFF vs kF), then **these reactions occur faster and more intensely in the presence of leucine in the G+L model** (k2 vs k1; k4 vs k3).

This kinetic model, although preliminary and simple, makes it possible to adequately describe the experimental concentrations and makes it possible to estimate the degradation of the precursors and the behavior of two hypothetical intermediaries (bell-shaped curves) *(ACL 4).*

What is interesting in this work is that we can **relate the appearance of reaction products to the temperatures measured where the reaction takes place, that is to say on the surface of the cakes.** Indeed, in model G, furfural is detected after 34 min of cooking. This corresponds to high temperatures on the surface of the product (139 ± 2°C), which can trigger caramelization, the only thermal reaction supposed to occur in model G. These results are therefore consistent with previous studies on simple model systems showing that the caramelization reaction requires a temperature higher than 120°C for the degradation of glucose *(Hurtta, Pitkänen & Knuutinen, 2004; Kroh, 1994)*. On the other hand, in the G+L model, the presence of leucine seems to favor the earlier generation of furfural which is detected at 10 min, corresponding to much lower surface temperatures (100 ± 5 ° C).

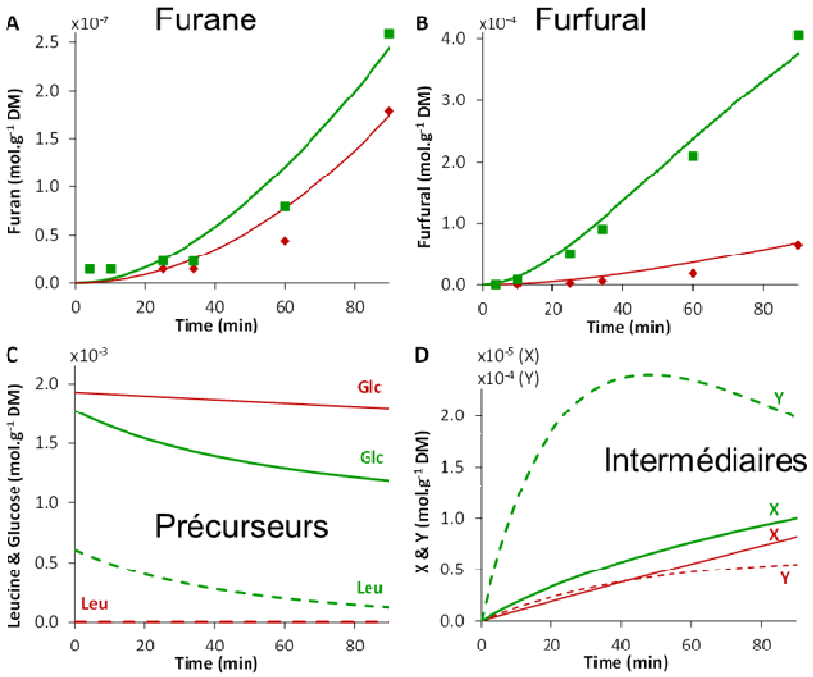


Figure 36: Kinetics of furan and furfural formation generated by cooking at 170°C in model sponge cakes accompanied by the consumption of precursors and two intermediates. Model G (in red) and model G + L (in green)). The discrete points represent the experimental points and the dotted curves the modeling. Adapted from *(ACL4).*

These results show that, **under caramelization conditions, glucose is unlikely to form furan,** when it leads to non-negligible amounts of furfural. With the addition of leucine, the Maillard reaction is activated at lower temperatures, resulting in very high concentrations of furfural, while the furan concentration always remains low until the end of cooking. This seems to suggest that 1,2-enolization is favored over the 2,3-enolization pathway under these conditions of reactivity (T, nature of the precursors).

These results show us the interest of having quantitative data to access the rate constants and the need to have experimental data on key intermediates such as dicarbonylated compounds (1-deoxyosone, 3-deoxyosone in particular).

Towards a more complete reaction scheme for modeling

The analytical effort deployed during the PhD thesis of J. Lee, allowed us to study the influence of the composition of precursors and cooking parameters on the reaction kinetics during the cooking of G and G+L model products.

The diagram of the reactivity induced by the presence of these two precursors is shown in *fig. 37*, all the dosed markers being highlighted in different colors. This scheme, not so simple even if arising from only two precursors, is an observable scheme, that is to say that the assay of the markers chosen will make it possible to identify and discriminate the different reactions, according to the Reactial methodology previously presented in this chapter.

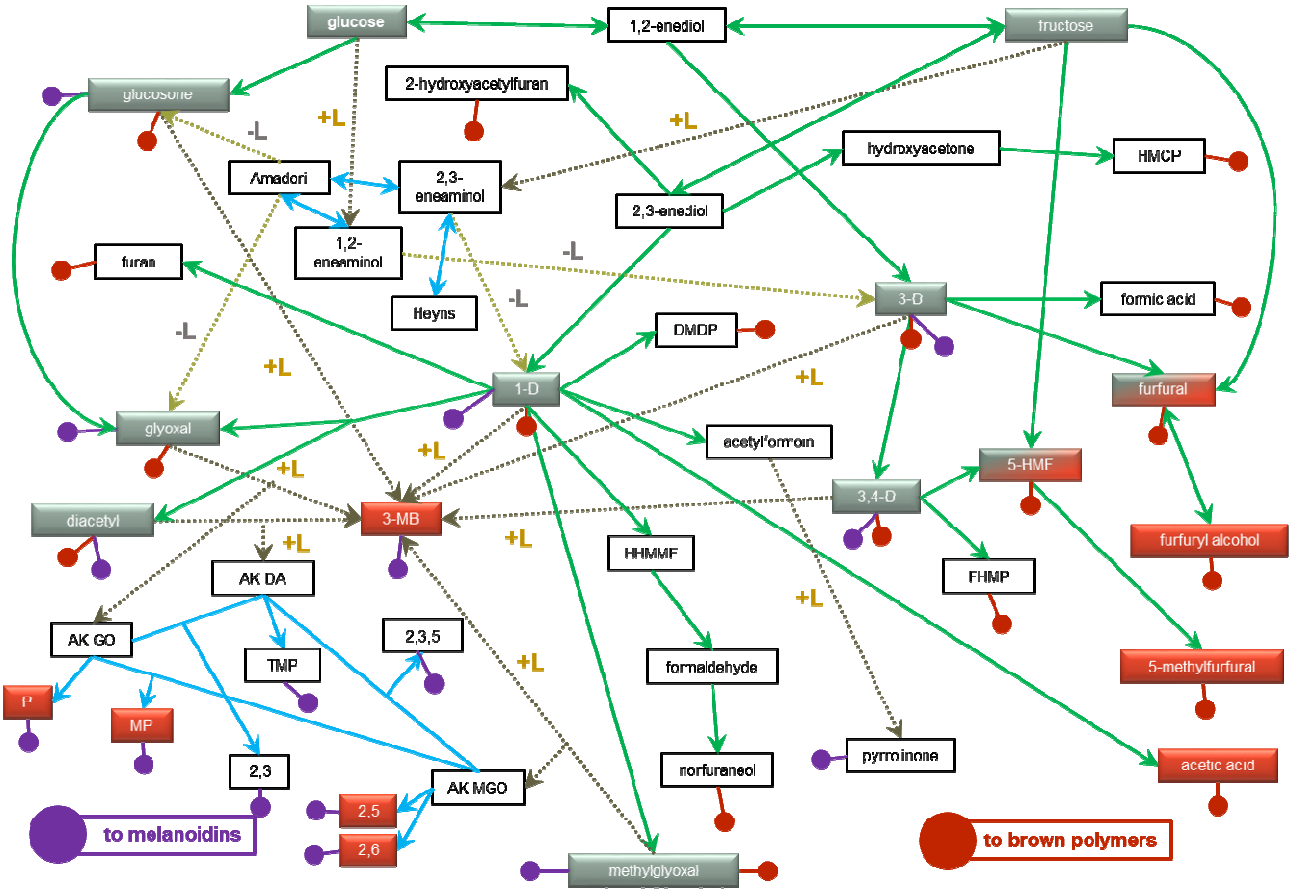


Figure 37: Simplified reactivity scheme of the G + L model product. The sugar degradation pathways are indicated in green; the dotted lines indicate the paths which involve the presence (in gray) or the consumption (in brown) of leucine; the routes in blue are those of the formation of pyrazines downstream of the degradation of Strecker. The measured markers are illustrated by a colored rectangle according to the sampling method: in gray - extraction of the matrix - and in red - online extraction of cooking vapors. Furfural and HMF are dosed in the two compartments.1-D : 1-déoxyosone; 3-D : 3-déoxyosone; 3,4-D : 3,4-didéoxyosone; 3-MB : 3-méthylbutanal; P : pyrazine; MP : 2-méthylpyrazine; 2,5 : 2,5-diméthylpyrazine; 2,6 : 2,6-diméthylpyrazine; 5-HMF : 5-hydroxyméthylfurfural. D'après la thèse de J. Lee *(Th5)*.

The objective of J. Lee's PhD thesis was to kinetically assess what is the combined influence of process (3 cooking temperatures, two levels of forced convection) and the presence of two specific precursors (glucose and leucine) on the chemical reactivity of the model sponge cake. The strategy was to conduct the acquisition of kinetic data in thin products, and the acquisition of thermal data in thin and thick products, in order to couple the stoechio-kinetic model from the observable scheme with the heat and mass transfer model *(fig. 38).*

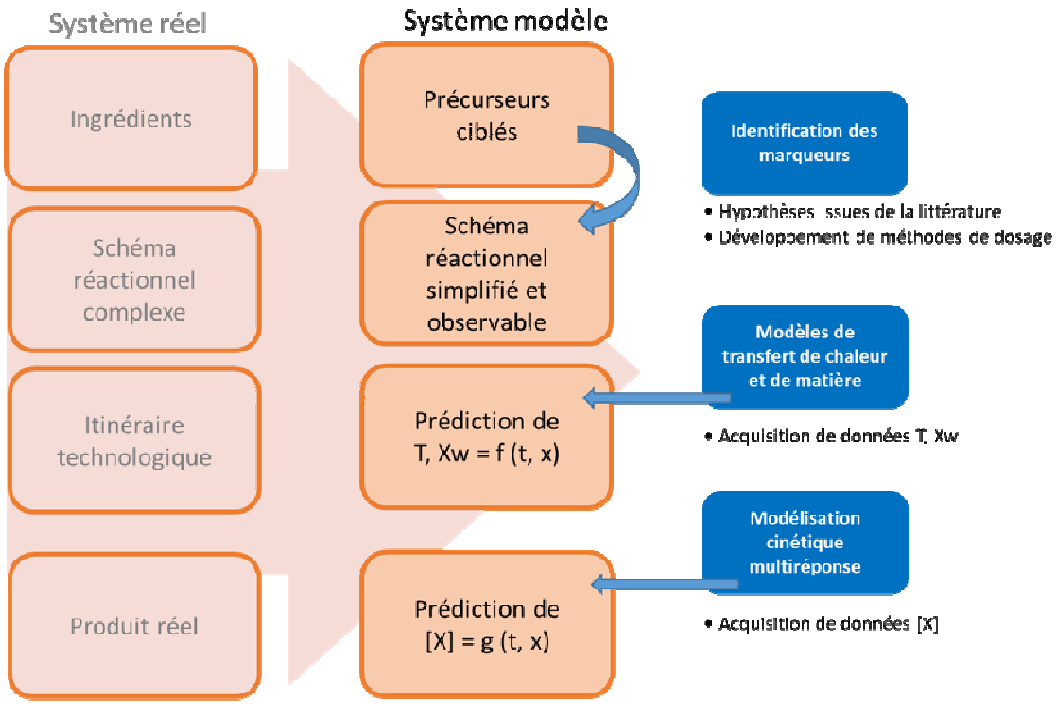


Figure 38: Experimental strategy for the thesis of J. Lee. Adapted from (Th5).

First of all, it is interesting to note, in a completely macroscopic way, that the browning is weak and slow for the sponge cake G when it becomes very fast and very intense for the sponge cake G + L, as illustrated by figure 39. This gives an idea of the acceleration of browning reactions in the presence of leucine. But the more interesting results come from the kinetic analysis of markers.

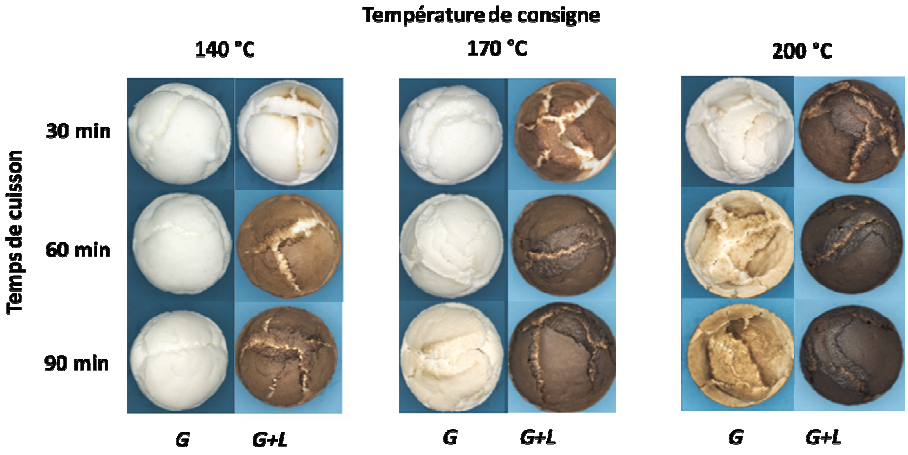


Figure 39: Browning of models G and G+L at 3 temperatures and 3 different cooking times. According to the PhD thesis of J. Lee.

Figure 40 shows the fate of the precursors and intermediates at the three temperatures. In the presence of leucine, glucose is consumed much faster and the faster the temperature is high. Also the carbonyl intermediates 3-deoxyosone and 1-deoxyosone are formed in much larger amounts in the presence of the amino acid. The bell-like appearance of these intermediates clearly shows that there is both the formation and degradation of these compounds, with consumption being all the more accelerated as the temperature is high.

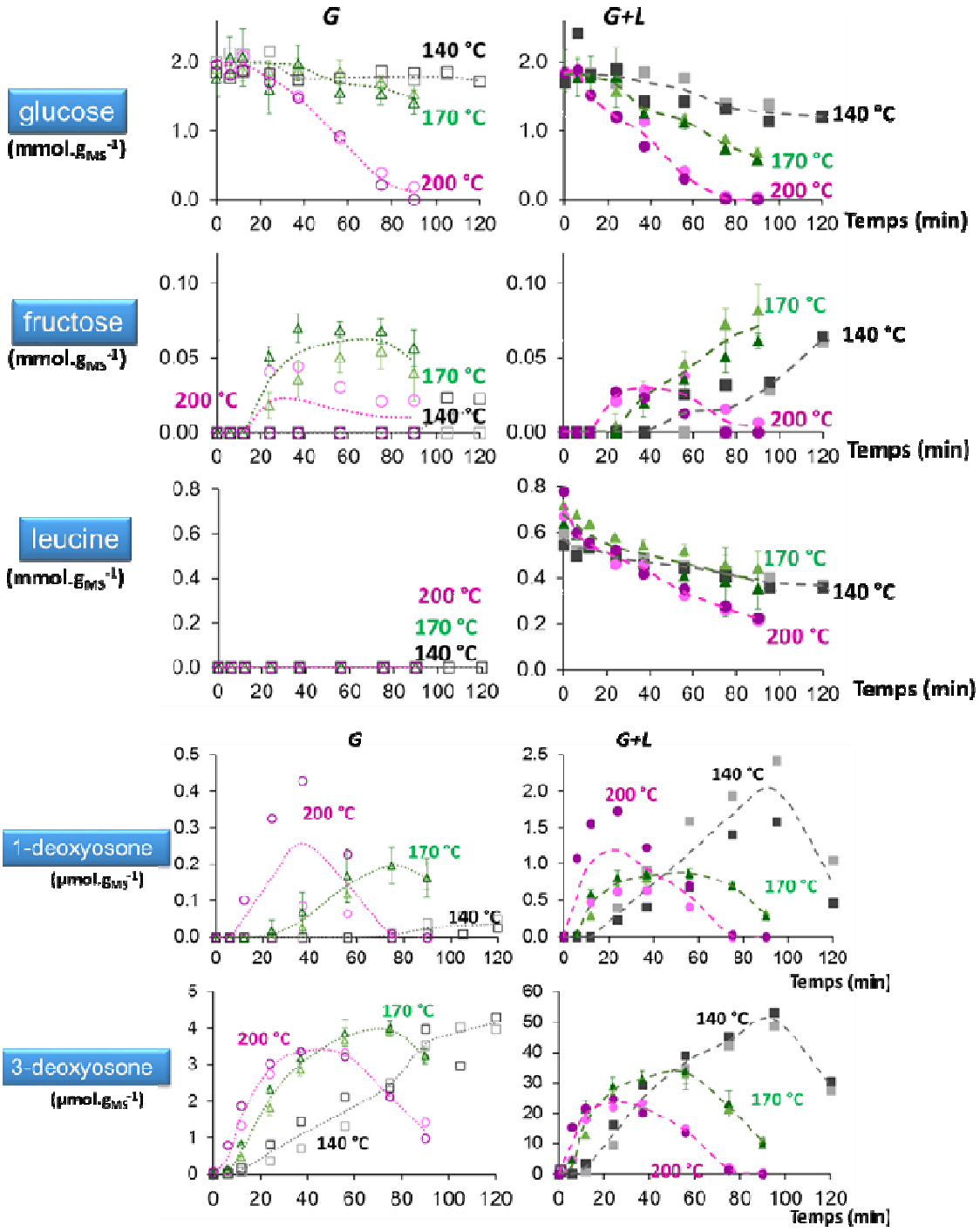


Figure 40: Kinetics of consumption of the precursors and intermediates in the G and G + L model cakes at the three cooking temperatures (140°C, 170°C, 200°C). Sponge cake model G (empty symbols) and G + L (solid symbols) at 140 ° C low convection (□,■,n=1), 140°C high convection (□,■,n=1), 170°C low convection (△,▲,n=3), 170°C high convection (△,▲,n=3), 200°C low convection (○,●,n=1) and 200°C high convection (○,●,n=1 The lines show the trend for each temperature considering the two convection levels as repetitions. Adapted from the thesis of J. Lee (Th5).

If we focus on some selected reaction products such as furan and Strecker's CNFVs *(figure 41)*, we observe the non-linear accelerating effect of temperature on the formation of volatile markers, with curves typical of the law of Arrhenius, whatever the nature of the markers and precursors (G and L). Again, in the presence of leucine these compounds are formed faster and in higher amounts. It is interesting to remember that we pushed the kinetics much further than under the conditions applied in the study of Srivastava (ACL4), until we observed the consumption / degradation of the furan compounds after 80 min of cooking at 200 °C. This

could be linked to the involvement of these compounds in the formation of brown polymers because at these cooking levels the browning is very intense *(fig. 39).*

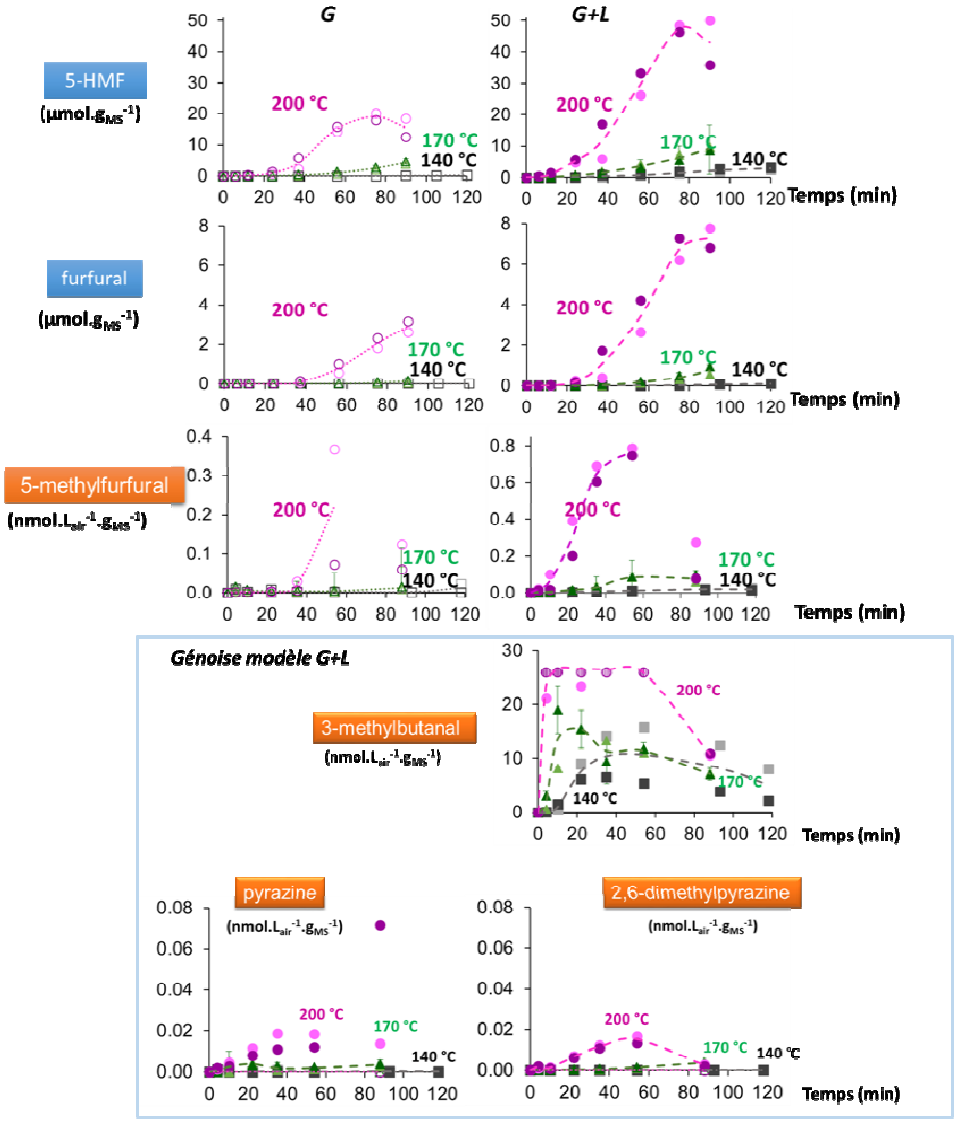


Figure 41: Kinetic formation of markers dosed in products by UHPLC / DAD (blue label) and in cooking vapors by TD-GC / MS (orange label). Sponge cake model G (empty symbols) and G + L (solid symbols) at 140 ° C low convection (□,■,n=1), 140°C high convection (□,■,n=1), 170°C low convection (△,▲,n=3), 170°C high convection (△,▲,n=3), 200°C low convection (○,●,n=1) and 200°C high convection (○,●,n=1 The lines show the trend for each temperature considering the two convection levels as repetitions. Adapted from the thesis of J. Lee (Th5).

These results irrefutably confirm that the addition of leucine in the G + L model makes it possible to activate the Strecker's degradation pathway and all the pathways where leucine is necessary *(fig. 37).* The products of this route (3-MB, P, MP, 2,5-DMP and 2,6-DMP) were indeed found exclusively during the baking of the G + L model. In particular, 3-MB, Leucine-specific Strecker's aldehyde, forms very quickly and in large quantities compared to other SD products, even under the mildest cooking conditions (140°C).

I could summarize the reactivity of these model products in the following terms: under caramelization conditions (model G), the glucose isomerization pathway via 1,2-enediol seems preponderant, because the system mainly evolves towards relatively large quantities of fructose and 3-D, with similar dynamics. Caramelization is strongly activated by temperature and we observe an almost total consumption of glucose at the end of cooking at 200°C. However, it leads to less intense browning than in the system (G + L). By adding leucine to our system, **the Amadori's rearrangement is very rapid**, probably via the formation of 1,2-enaminol, **promoting the formation of 1-D in addition to 3-D**. These channels are activated at lower

temperatures than those necessary to initiate caramelization. In this system we identified a **strong activation of the Strecker's degradation** via the consumption of dicarbonyl intermediates. The convergence of several reaction pathways towards the formation of 3-MB could explain its strong accumulation in the product.

These results confirm the previous results obtained from a thick model cake baked at 170°C *(ACL4).* In that work we could find the same trends and concentrations for precursors (set), furfural (measured) as well as the intermediate Y (estimated) corresponding to 1-D. A difference is noted for the intermediate X (estimated) corresponding to 3-D which is found here at concentrations 10 times higher in the presence of leucine and whose shape is not curved *(fig. 36 vs fig . 41)*. This could be due to the neglect of other active reaction pathways which both generate and consume 3-D causing this parameter to be underestimated in the simple kinetic model proposed by R. Srivastava *(ACL4).*

To conclude, these kinetic results allowed us to constitute a **rich robust and reliable experimental database for modeling**. We have also been able to extract an observable reaction scheme which succeeds in discriminating the caramelization and Maillard reaction pathways. Two proofs of concept (POC) of coupled models were carried out for formula G. The first POC taking into account all the markers for a single cooking condition, the second consisting in predicting the degradation of glucose for all cooking conditions. The results are encouraging for the continuation of the modeling work. This part will be continued in the context of an external collaboration providing the appropriate technical skills for the development of the adapted calculation algorithm.

Highlights of axis III

1. We have successfully applied a reaction engineering approach to **the study of reactivity in solid food products** having different degrees of chemical complexity.
2. This approach makes it possible to follow **the fate of reaction markers linked to the quality of the product and in connection with mass and energy transfers**, in the product being transformed during cooking.
3. We have developed a **solid model product which allows us to control reactivity** and structure, while following the same technological route as that of a real product.
4. By enriching this model product with specific precursors, we have succeeded in **decoupling the caramelization and Maillard reactions** and in characterizing their kinetics throughout the cooking.
5. We have constructed a **very complete observable scheme** for one or two precursors (glucose, glucose and leucine). The identified reaction pathways were validated by the experimental kinetic results.
6. We have acquired **a large database** (kinetic and thermic data) under **strictly controlled process conditions suitable for multi-response kinetic modeling.**

Professional development and promotion aspects

7. **I developed and applied my expertise on the dynamics of thermal reactions** to multidisciplinary projects, at the interface between food science, analytical chemistry and process engineering.
8. I participated in the **co-supervision of 3 ambitious and multidisciplinary PhD thesis projects**. Thanks to this training through research, these doctoral students pursued careers in higher education, research or innovation management.
9. We valorized the original results obtained in solid model by **3 ACLs** (2 in finalization), **3 ACTs and 5 oral and poster communications.**

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Chapter 3

Summary of teaching activities and links with research

Chapter 3: Summary of teaching activities and links with research

Participation in the teaching of the establishment and main achievements

My lessons are carried out as part of a service of 100% lecturer in food chemistry within AgroParisTech, **department SPAB** (Sciences and Processes of food and bioproducts). This department covers a broad disciplinary spectrum: biochemistry, chemistry, physico-chemistry, microbiology, process engineering, modeling, sensory analysis and consumer sciences. It represents a working community of 160 permanent staff (including around 40 teachers researchers) attached to two joint research units (Unités Mixtes de Recherche- UMR) (mainly SayFood - Paris-Saclay Food and Bioproduct Engineering Research Unit and Micalis - Food microbiology for health) and a unit of research and development (ABI - industrial agro biotechnologies).

My teaching activity is **strongly linked to my research activities** because it is part of the disciplinary field of food chemistry and specifically concerns aspects relating to the properties, reactivity and analysis of molecules of interest (i.e. food flavors) as well as food safety linked to chemical risks. **Most of my teaching activities are dedicated to the Erasmus Mundus Joint Master Degree Food Innovation and Product design "EMJMD FIPDes" of which I am the general coordinator since its creation in 2010.** For the educational objectives of this new training, I have created and implemented numerous lessons in English focused on the contributions of food chemistry to the design, formulation and safety of food products in collaboration with my French and European colleagues.

The overhaul of the AgroParisTech curriculum in 2010 and the creation of the FIPDes program in 2011 were the occasion for a profound renewal of all my lessons (approx. 90%). In addition to the consolidation and improvement action resulting from these reforms, I actively participated in the implementation of the new master offer in 2015 within the new framework of Paris-Saclay University with the creation of the international FIPDES course owning to the Nutrition and Food Science Master NSA, which brings great international visibility to establishments. My implication in teaching was very important in particular with the creation of many courses, projects and approaches adapted to very different students (international curriculum, transversal and multidisciplinary lessons) in English. This implication resulted in a congruent overshoot of statutory hours until 2017 when I focused my activity on the FIPDes Master and took responsibility for the CAliPro research team until 2019.

The summary of my teaching activities is given in *annex 7*. In the next section I will detail a small part of them.

MSc. Eng. Curriculum

In the second year of the Engineering MSc., I take part in several lessons focusing to quality, health safety, additives and food flavors in the frame of the AgroParisTech thematic area 2 and 4. My activity therefore concerns more specific aspects of food chemistry closely linked to my research activities in the field of **food flavorings and newly formed compounds with organoleptic and / or health impact.** Particularly in the EU "Food additive and flavorings", I created a TP on the interaction between food flavors and matrices and I supervise TP students on such a subject.

I also contributed to the **creation of a multidisciplinary module in English on risk assessment and management throughout the food chain** "Food Safety in the food chain". This course, for which I am also co-responsible, is an elective module, one of the only in English available for AgroParisTech Eng. students and open to international students (Erasmus and FIPDes). This new offer has been greatly appreciated by engineering students who can therefore mix with international students (and vice-versa). During the last editions we have set up a panel (round table) on the challenges of health security and quality in food

innovation that I co-led and co-organized in its first two editions. The students prepare the round table and ask different questions to renewed guests (national and international) from the most innovative sectors of the food industry (distribution, emerging sectors) such as the head of Food Safety at Amazon UK, the CEO of 'Ynsect", the president of Spiruline producers de France, etc. trying to balance large structures, SMEs and startups. We open this panel to the entire promotion of FIPDes (25 students) for a maximum impact. This is **an example of Internationalization at Home action driven by the European Commission**, which we apply through joint activities to local and international students.

In the third year, I contribute to the module "Food flavorings: formulation and implementation" of the study track "Product Design and Development" with a master course on the interactions between food flavors and matrices by addressing the complexity of physicochemical interactions and the reactivity of the matrix with a view to formulation engineering.

Postgraduate education

My activity takes place within the framework of the new master's offer from Paris Saclay University. Within the BASE School (Biodiversity, Agriculture and Food, Society, Environment) I intervene in the **Nutrition and Food Sciences (NSA) Master,** mainly for the international course Food Innovation and Product Design Erasmus Mundus Joint Master Degree (FIPDes) and, to a lesser extent, for the Food Health Risk Analysis (ARSA) course. For the latter I provide a masterful course on the heart of my research activities, on the **food safety issues related to the presence of newly formed compounds in processed products.**

As part of the **Specialized Master AgroParisTech Executive** "Products Engineering at the Kitchen-Industry Interface" (IPCI), I intervene with lectures and practical on the **formulation of flavored foods**.

Erasmus Mundus Joint Master Degree FIPDes (M1 et M2)

The Master FIPDes is a 2-year academic program in the field of Science, technology and innovation. Its objective is to **bring a European dimension** in food innovation and product design education to better respond to the global challenges of the Bioeconomy. FIPDes trains the next generation of executives able to work across borders, with an inclusive vision of innovation, in order to provide sustainable and healthy solutions for feeding future generations. It is an interdisciplinary training dedicated to students from countries around the world. This is a joint program coordinated by AgroParisTech in collaboration with the Technical University Dublin - Ireland, The University of Naples "Federico II" - Italy and the University of Lund - Sweden. Students conduct their studies in two or three establishments depending on their interests (compulsory mobility specific to the Erasmus Mundus program) (www.fipdes.eu).

The lessons delivered by AgroParisTech are based on the strengths of the SPAB department. The strong points of this project are to widely apply an **inductive pedagogy (work by project),** to use the dynamics of international exchanges, to widely involve industrial partners from the R&D sector, to develop transversal and transnational modules. More than 20 institutional, industrial and non-governmental associate members also contribute to this program by making it a training program with worldwide influence. The idea is to bring together universities and international research groups to create a **unique master's degree which does not exist at national levels**. More than thirty teachers and researchers from AgroParisTech (SPAB) are involved for a total of two full semesters of courses delivered in English (mostly creations).

Since 2011, I have been very active in teaching in this training, being passionate about innovative teaching methods adapted to a public which is very different from classical engineering and master students, while continuing my mission of local and international coordination. My **missions are therefore deployed in terms of pedagogical coordination, teaching and strategic coordination and management of the program.**

Teaching activities (in English)

-Design of modules, evaluation devices, and innovative transversal activities between the different Partner Universities.

- Design and production of multidisciplinary and transversal projects and learning activities.

- Coordination of pedagogical quality assurance

Here are the main educational creations and the most significant developments:

M1 FIPDes

☞ Following the expression of the need within the student and International Advisory Board, I created the Teaching Unit "**Introduction to formulation engineering applied to food products**" (24h). It is a multidisciplinary course (texture, aromas, nutrition, regulations, statistics, formulation) to provide students with the basic knowledge, methodologies and tools for a reasoned approach to formulation with a view to the industrialization of food products (transition from recipe to pilot tests), including understanding the essential aspects of the European regulatory framework and labeling policy. I take care of the coordination of this course (expert conferences, industrial visits) and I organize a day of experimental workshops on flavoring, colors and labeling. As a learning and evaluation tool, I developed an integrative mini-project based on a team game ("Chimera Spec game"). This course arrives at the end of the first semester and is an opportunity for students to integrate everything they have studied in previous modules. For this, I introduced in this course a self-evaluation activity of student innovation projects related to the transversal modules over the two years and between AgroParisTech and Technical University Dublin. To do this, I developed with the help of the innovation engineer FIPDes a support tool for the formulation **("FIPDes Innovation Toolbox"**) via the digital platform TICE of the master. This tool will serve as a hyphen and a "reflective" tool throughout their course.

☞ In terms of educational coordination, **I promoted the creation of the new Transversal Innovation Project I (TIP I) module: Intercultural Intelligence, Project Management and Creativity.** I firmly believe that the **multicultural richness of FIPDes students is a plus for creativity and therefore food innovation. I wanted this potential to be better exploited within FIPDes.** For this I also include specific educational activities to support the development of intercultural communication skills which are essential for tomorrow's executives, by calling on experts (Mitra +, now an associate member of FIPDes). This promotes the creativity activities which are organized by my colleague G. Yannou Le Bris. This module is developed transversally with Ireland where the Transversal Innovation Project II (TIP II) -Food prototype development and evaluation takes place: the innovative concepts worked on in France during this module will be developed in Ireland, then evaluated and, possibly , industrialized during the Senior Project in M2 (see following).

☞ I have made my courses evolve in the context of the Teaching Unit "**Comprehensive Food Science and Analysis"** on the chemical analysis of compounds of interest and the reactivity of food by mixing reverse class methodologies, highly interactive tutorials and course delivery refocused on the **integrative aspects of the discipline** and based on the digital tool in English CHIMACTIV + developed in 2017 by my colleagues at SPAB.

☞ I coordinate the **"FIPDes Week"** which takes place at the start of the semester for M1 and M2 FIPDes (www.fipdes.eu). It is a very innovative module in terms of its methods, content and learning objectives for international students. It is also an **introductory week for students in the presence of European partners, experts and international professionals.** New students take part in many activities on this occasion to introduce them to the program, present them with innovation-related issues, assist them in setting up in France and foster a team spirit essential to the smooth running of training.

M2 FIPDes

☞ I created and coordinate with my colleague M. Moussa the **“Senior project in Food Design & Engineering”** module, relying on a multidisciplinary team (processing, formulation, chemistry, microbiology, sensory…) and external professional speakers (scaling-up, flavoring, culinary aspects). **We have recently introduced more content and activities on industrialization and we have integrated this module more with the other educational activities of FIPDes (notably TIP I, TIP II, Formulation engineering, entrepreneurship).** We guide groups of FIPDes students in the evaluation, possible reformulation and industrialization of some prototypes from the TIP II carried out in Ireland. My investment in coordination and tutoring was very important until

2017 when we recruited an Engineer in charge of innovation projects for FIPDes who is very involved in all FIPDes projects (TIP I, TIP II, Junior Project, Senior Project).

☞Within the module **"Reaction Engineering applied to Food Products"**, I give a lecture and I coordinate the experimental project on the **links between reactivity and organoleptic quality in cooked products, directly related to my research**. I supervise a group of 9 students (mixed group of students from the FIPDes and the local master Engineering-Products-Process track). The project is based on an **active pedagogy where students gathered in teams are actors and decision makers of their experimental work** and must be able to define a research question and set up the appropriate experimental approach to answer the question, conduct the experiments, then interpreting, synthesizing and presenting the results.

Activities of International and institutional coordination

The creation and coordination of the Erasmus Mundus FIPDes master's degree was a very important turning point in my career. It involved developing from scratch the framework adapted to the standards of excellence of Erasmus Mundus on the one hand, agile governance with a Consortium of 4 European universities on the other hand, and, at the same time, all the lessons for a totally new audience of students (international, trained in different disciplines, with varying professional experience, with very demanding expectations), all this with a French and international team of more than 30 colleagues. This means, in practice, the application of new and appropriate teaching methods for a curriculum 100% in English and a great work of coordination at the level of AgroParisTech and the European Higher Education Area (EHEA).

As general coordinator, I took care with the help of two deputy coordinators (for M1 and M2) to achieve the learning objectives and the continuous evolution of the program to meet the present and future needs of employers of FIPDes graduates. Within AgroParisTech, for example, it was necessary to train and also sensitize the teaching teams to the needs and **specificities of this new audience** (e.g. training in intercultural communication), to motivate them to work differently and in English (12 modules only at AgroParisTech). **FIPDes was for me the opportunity to work with colleagues from other European and non-European Universities (Sweden, Italy, Ireland, Korea), to exchange good practices and to develop new approaches.** Two examples: (1) the development of the transversal module "Transversal Innovation Project" with Ireland, and (2) the introduction of entrepreneurship within FIPDes by putting French and European infrastructures at the service of the program.

In addition to the purely educational aspects, this very ambitious project (around 10 million euros in budget since 2011) asked me to **develop and apply new managerial skills** to: (1) chair the Consortium Committee (composed of representatives of 4 universities of FIPDes); (2) lead the International Advisory Board (composed of all stakeholders of the master as well as international experts from joint programs); (3) **imagine a "business model"** that allows the institutional and financial sustainability of the program beyond European funding (e.g. I was very involved in the development of partnerships with companies and I worked with the AgroParisTech Foundation to set up a **fundraising strategy** for academic grants, among others); (4) **disseminate the results** of the program (presentations at international conferences, coordination of all external communication activities) and (5) **share my expertise** within the European Higher Education Area where **I am now identified as an expert in joint programs** (participation and animation of workshops at national and international level for the Education, Audiovisual and Culture Executive Agency of the European Commission (EACEA), founding member of ProDeJIP, an association for the promotion of joint programs.

Finally, **I particularly worked on the administrative and financial consolidation of FIPDes within AgroParisTech** (integration into the curriculum, assimilation by the different support services) and I coordinated the **submission of three projects for (re) accreditation and financing by EACEA (2010, 2016 and 2019), which were all accepted for a cumulative amount of approximately 10 million.** The re-accreditation and EU support are an important step in the sustainability of the program because it gives us excellent visibility at the global level (Erasmus Mundus label of excellence) and meanwhile allows us to **consolidate the results** in terms of employability and impact in the different countries where graduates will go to exercise their missions after FIPDes whatever their role (education, research, innovation, development, business).

Thanks to all these actions**, I am very proud to say that FIPDes has become an international benchmark training not only for AgroParisTech and Paris Saclay University, but also for the European Commission which awarded it two very prestigious labels in 2017**: "EMJMD Success Story" and "Best Management Practice" (https://www.universite-paris-saclay.fr/fr/actualite/decoulez-la-video-du-master-erasmus-mundus-fipdes), which has increased visibility and reputation of the master and partner institutions.

Outlook

The new EMJMD FIPDes project approved and funded by Europe until 2024 plans to **develop and implement new digital tools that meet the specific needs to support the technical skills and entrepreneurial skills of students.** I will therefore develop a digital implementation strategy for FIPDes and share the results and good practices between HEI or serve as a playground for specific experiments. For example, within actions 1, 3, and 4 of the HILL project (Hybrid-Innovative-Learning-LAB) led by the SPAB department, we can once again use FIPDes as a laboratory for educational innovation for the implementation of digital for activities related to food innovation training. The collaboration between a HILL educational engineer and the FIPDes engineer in charge of innovation projects is being developed, notably within the framework of the Food'IN Lab of AgroParisTech.

To do this, **I recruited in 2018 a research engineer in digital pedagogical engineering** in charge of the following project: **"Upgrading the FIPDes Master by applying information and communication technologies (ITC) at the most relevant scale".** It is first about understanding the educational needs of learners and teachers and proposing an appropriate digital action plan as well as the project roadmap. Then **pilot** the **design, development and implementation of multimedia teaching tools appropriate for FIPDes** and at the same time promote the evolution of teaching practices via digital with specific support and training for users (teachers, students) and a **setting in place of a continuous improvement approach with indicators of success**.

Global reflection of the link between teaching and research

The previous examples show how my teaching activities are connected to my research and how they feed each other. *Figure 42* provides a graphical summary, with emphasis on the complementary aspects and the link to innovation.

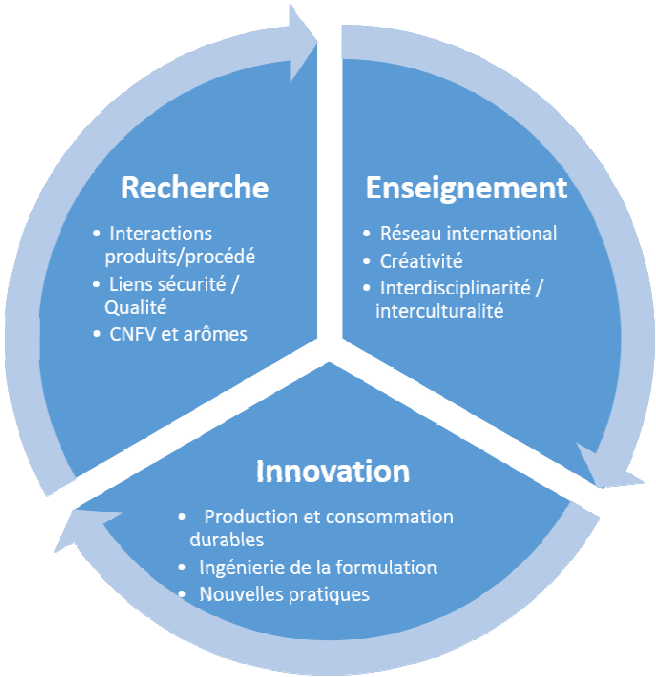

Figure 42: The Knowledge Triangle transformed into a circle: increased circulation and cross-fertilization promise!

Two strong points emerge during my career as a teacher-researcher:

1- Teaching side: an exciting, intense and very fruitful activity of creation, coordination and consolidation of the international master FIPDes.

The past few years have been very formative. I learned to coordinate an international training program and I got to know all the administrative departments of their interior and work very closely with them. I learned to manage teams with different specificities with all aspects of personnel management that were completely foreign to me (recruitment, financial management, partnerships). The pedagogical coordination at the level of AgroParisTech allowed me to interact and work in a team with many colleagues (around thirty EC intervene in the courses at APT). I really appreciate this role which requires great listening and a great propensity for cooperation.

But, more than anything else, **I appreciate my mission of animation of the international consortium FIPDes**, because I manage to work in a constructive, enthusiastic and dynamic climate with my European counterparts according to the principle of participative management. We have accomplished great things and today I am proud to see that the FIPDes program has become a **success story of Erasmus Mundus**.

This program was a golden opportunity for the internationalization of AgroParisTech. There is still a lot to do and I hope that the establishment can capitalize on all of this investment. This EMJMD Master has been accredited and funded by EACEA since 2010 and until 2024, without discontinuity. This implies great responsibility for continuing to achieve the high quality standards required, with a view to short-term financial autonomy.

For the future, I intend to continue to represent the establishment at various international and national meetings. A major project, for example, is the creation of a joint diploma. We have reached the first stage of this process with in particular the creation of a FIPDes establishment diploma and now we are in the process of instructing the FIPDes joint diploma, after a slowdown due to the creation of the University of Paris Saclay and from Technical University Dublin.

2- Research side: The dynamism of international projects and a renewed research environment

Thanks to the expertise acquired following the thesis work of M. Cepeda Vazquez and J. Bousquières and to my taste for international relations**, I had the opportunity to start a new collaboration** with European universities and industrial partners from **ITN Food Engine project** (Enginomics in food quality design: the case of shelf-stable fruit-, vegetable- and legume-based Foods). This project, coordinated by KU Leuven, advocates a multi-response kinetic approach for the modeling of quality indicators of food products, coupled with sensory properties and consumer preferences. In this context I am **co-supervising with C. Bonazzi the thesis of Svenja Krause** (Evaluation of the use of legume-based ingredients in processed plant-based products) which started in October 2018 (see chapter 5). The program took advantage of the opportunity to **recruit excellent international candidates, including FIPDes graduates.**

Within the **newly created SayFood UMR**, I am therefore now part of the **new GéPro team (Product Engineering)** which brings together the expertise of the Calipro and SP2 teams (chemistry, biochemistry, process engineering, biomaterials science). The GéPro team aims to develop tools and knowledge for the reasoned construction of the properties of processed products. It positions itself on the question of the couplings between structuring processes and reaction dynamics at work during the processes, and on the importance of these couplings in the construction of the properties of the products produced. To understand the mechanisms involved, we will also sometimes have to work specifically either on structuring processes, or on reaction dynamics, under controlled conditions and on model systems.

Here again **Research, Teaching and Innovation will be at the heart of our activities by welcoming interns whom we have trained in our master's specialties such as Product and Process Engineering or Food Innovation and Product Design,** as in the context of the collaboration for the internship from Eugenia Asamoa currently underway on functionality and reactivity of new pea-based ingredients.

Chapter 4

Research management activities

Chapter 4 : Research management activities

The animation of the research that I developed was organized around three guiding principles which have gradually been deployed since I took up my position as teaching researcher at AgroParisTech (initially ENSIA) in 2004. First of all, supervising interns and PhD students. Second, the management of research projects of different sizes, durations and levels of responsibility. Finally, collective animation within the UMR and more generally of AgroParisTech. I conducted these research activities in parallel with my teaching duties, which became very sustained in 2010 with the setting up and coordination of an international Erasmus Mundus Master program. These two missions feed each other from the point of view of scientific expertise (cross-fertilization between teaching and research subjects) but also concerning the experiences of collective animation and responsibilities of a complex project. This dynamic is illustrated in *Figure 43* which, in chronological order, reveals the most significant experiences.

Supervision

Since 2004 I have **co-supervised 6 PhD theses**. *Figure 44* summarizes their contribution to the 3 lines of research presented in Chapter 2. *Table 2* summarizes the valorisation resulting from this work (only co-signed publications) and gives an estimate of my real involvement in the supervision of work. The professional future is also indicated, PhD doctors have very easily found a job in France or abroad. The thesis of S. Fehaili was carried out within the framework of the ANR Reactial project and gave rise to an article in an international journal with reading committee. S. Fehaili is now a lecturer in food process engineering at SUPBIOTECH. S. Deterre's thesis focused on understanding the stages in the preparation of bitter orange distillate on the chemical and organoleptic quality of the latter. My role was to supervise part of the work on the identification of odoractive compounds in the different fractions of the distillate. This CIFRE thesis, conducted in collaboration with Grand Marnier-Lapostolle, gave rise to 4 ACLs, 2 of which are co-signed. However, this work is not detailed in Chapter 2 by deliberate choice to focus on the theme of CNFV in cooking products. I emphasize that this thesis opened the way to 5 other theses supervised by my colleagues P. Giampaoli and M. Esteban-Decloux. S. Deterre, after a post-doc at Mars and the setting up of an American start-up, is R&D manager in the area of expertise of his thesis (distillation). J. Bousquières' thesis, carried out as part of a DIM project, resulted in 4 articles, 2 of which were co-signed with me. J. Bousquières is now responsible for innovation for a French start-up in the energy optimization sector but wishes to return to R&D. Mayela Cepeda Vasquez worked as a research engineer in digital educational innovation at AgroParisTech under my direction between 2018 and 2019. She has just been hired by Agilent-Spain, as project manager. Mayela Cepeda Vazquez's thesis gave rise to 4 ACL, all co-signed. J. Lee has just defended his thesis in December 2019. We have co-published 1 ACL and 4 others are submitted or being finalized. J. Lee is currently a contractual lecturer in process engineering at AgroParisTech until August 2020. In addition to the thesis projects, we must not forget the students I have supervised either to support the work of doctoral students or to lead parallel or independent projects: 15 internships at Master level and 5 interns at BTS/license level. *Annex 5* exclusively summarizes work at the master level. To conclude, it should be emphasized that the EMJMD FIPDes Master constitutes a source of excellent international candidates, the most passionate of whom are recruited for a thesis in our UMR (3 to date), for example during European projects such as the MSC-ITN- Foodengine.

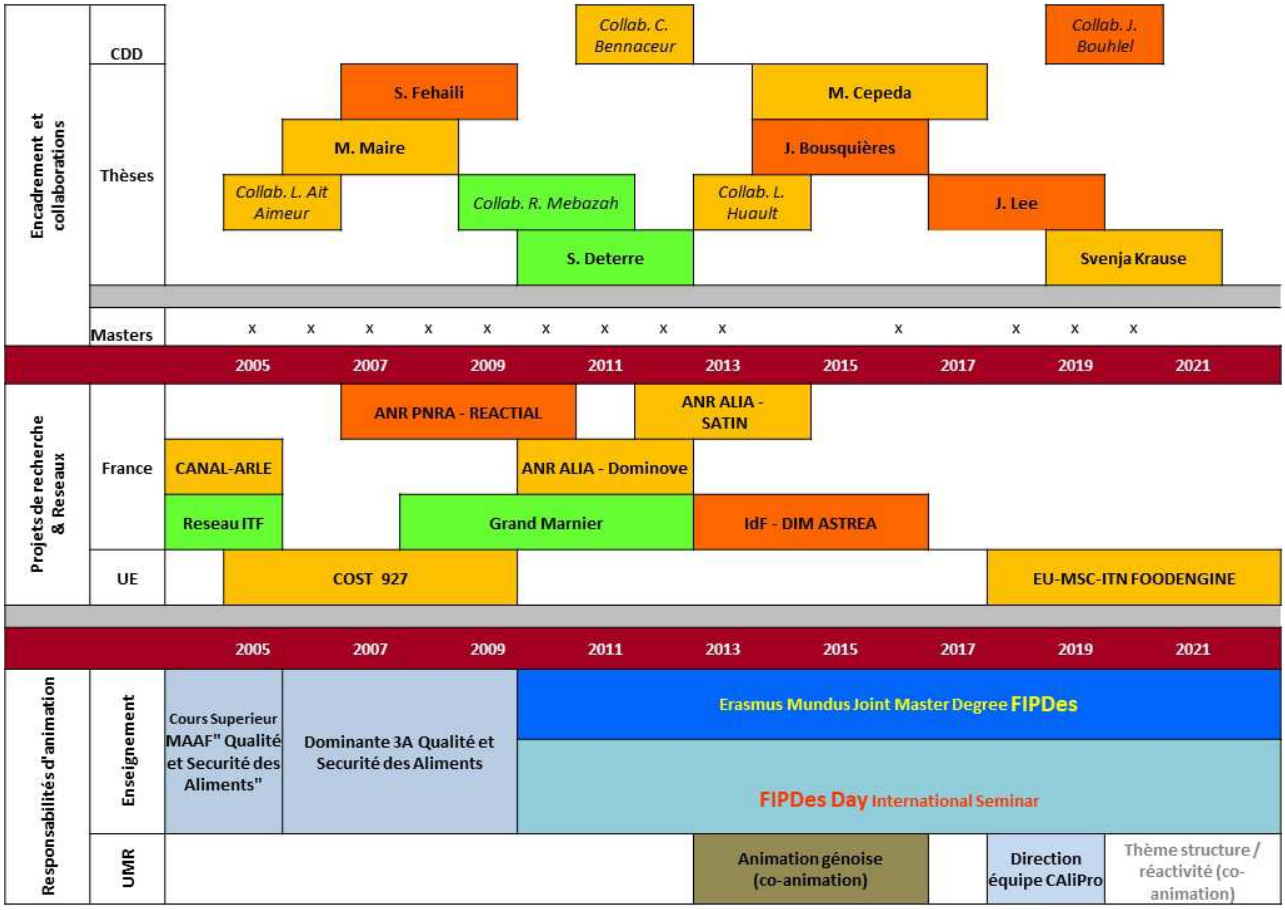

Figure 43 : Chronology of supervision, research projects and main leadership responsibilities. The same colors indicate close research questions. In green the questions related to the formation and becoming odoractive compounds, in yellow the questions of reactivity / process / formulation interactions, in dark orange the kinetic studies on real or model products. CDD: short term contract as a contractual lecturer and research engineer.

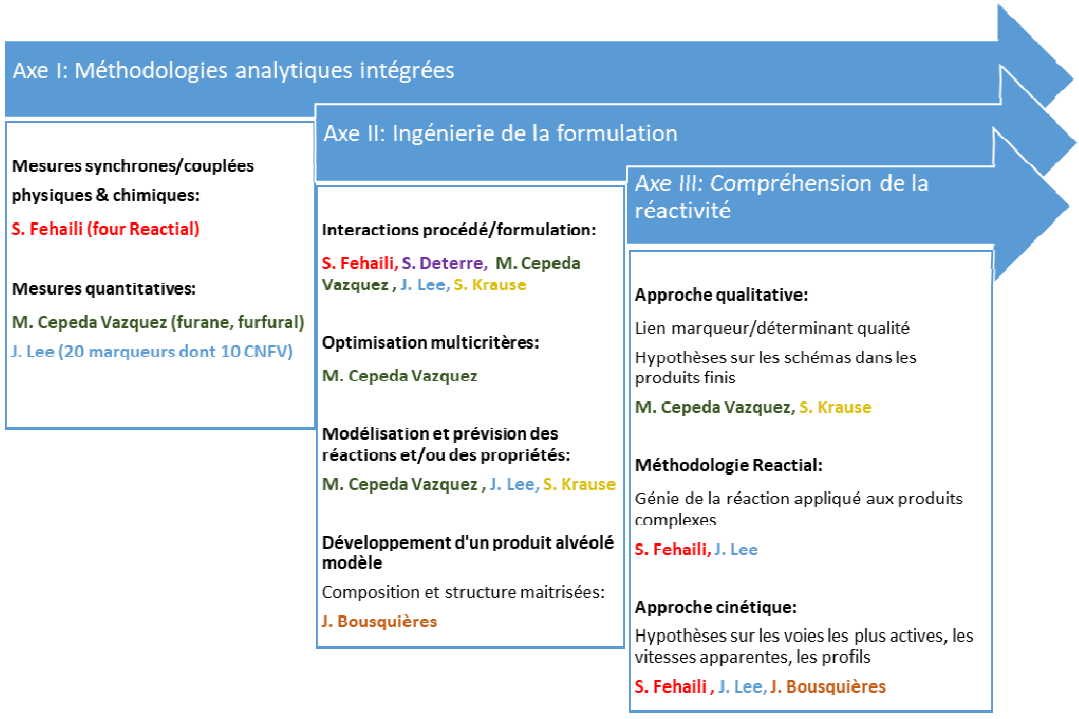

Figure 44: Contribution of the 6 doctoral students to my research activities as presented in chapter 2. The color code is used to differentiate doctoral students.

Table 2 : List of doctoral students co-supervised with some details on their current profession and valorisation.

Doctorant	Titre de la thèse	Financement	% Encadrement (expertise)	Période	Devenir professionnel	Valorisation (articles co-signés)
Souad Fehaili	Développement d'un simulateur de cuisson pour l'étude du couplage entre les transferts d'énergie et de matière et les cinétiques de réactions de Maillard ayant lieu au cours de la cuisson de produits céréaliers de type génoise.	ABIES	**30% B. Rega** (chimie) 40% P.Giampaoli (chimie) 30% M. Courel (g. des procedés)	2006-2009	Maître de conférences SUP BIOTECH	**1** Publication: ACL12 Congrès: **4** Publications d'actes: ACT1, ACT2, ACT3, ACT4, Poster18, Poster19, O7
Sophie Deterre	Comprehension des mecanismes phys cochimiques ayant lieu lors de la production d'un distillat d'orange. Rôle des différentes étapes d'élaboration sur la qualité chimique et organoleptique du produit fini.	CIFRE Grand Marnier	**20% B. Rega** (chimie) 40% P.Giampaoli (chimie) 40% M.Decloux (g. des procedés)	2009-2012	Responsable Conception et Développement DISTILLERIE BOINAUD	**4** Publications dont 2 cosignées: ACL7, ACL9 Congrès: Poster20, Poster21, Poster22 **3** conf. Orales
Josselin Bousquières	Impact de la composition et des procédés sur la réactivité d'un produit modèle alvéolé.	Région Ile de France	**20% B. Rega** (chimie) 40% C. Bonazz (g. des procedés) 40% C. Michon (biophysique)	2013-2016	Chef de Projet Innovation, EVOLUTION ENERGIE France	**4** Publications dont 2 co-signées: ACL1, ACL4 Congrès: **5** posters dont 2 cosignés: Poster12, Poster13 **4** conf. Orales
Mayela Caseda Vazquez	Rôle des ingrédients et des précurseurs réactionnels sur la génération de marqueurs moléculaires liés à la qualité sanitaire et sensorielle d'un produit céréalier de type cake	Conacyt Mexique	**50% B. Rega** (chim. des aliments) 50% V. Camel (chim. analytique)	2013-2017	Chef de Projet Analytique, AGILENT Espagne	**4** Publications: ACL2, ACL3, ACL4, ACL5 Congrès: Poster5, Poster8, Poster9, Poster10, Poster11, Poster13, **3** conf. Orales: O3, O4, O5
Jeehyun Lee	Analyse et modélisation de la réactivité au cours de la cuisson d'un produit modèle mimétique d'un produit céréalier type génoise	ABIES	**40% Rega** (chimie) 40% C. Bonazz (g. des procedés) 20% S. Roux (g. de la réaction)	2016-2019	Maître de conférences AgroParisTech	**1** Publication: ACL1 **4** ACL en preparation Congrès: Poster2, Poster3, Poster4, **2** conf. Orales: O1, O2
Svenja Krause	Evaluation of the use of legume-based ingredients in processed plant-based products	EU-MSC-ITN	**50% Rega, co-direction** (chimie) 50% C. Bonazz (g. des procedés)	2018 2021	En cours	

Setting up, participation and scientific coordination of research projects

I participated in the conception of the Reactial project in 2006, of which I was also the scientific coordinator for the UMR SCALE:

Projet ANR Reactial (2007-2010)

Title : *Prediction and control of the appearance or disappearance of reaction markers during food processing and preservation.*

Funding : ANR (Agence Nationale de la Recherche)

Coordination : C. Bonazzi (UMR GENIAL)

Parteners : UMR GENIAL, UMR SCALE, UMR SQPOV, UMR IATE, UMR QUAPA, LGC - Laboratoire de Génie Chimique, UMR 5503, Fromageries Bel, CTCPA, moulins Soufflet, WUR.

My role : responsable scientifique pour l'UMR SCALE ; contributeur au WP2,WP3, WP4 (thèse S. Fehaili)

Summary : The objective of this project was to develop a methodological approach to building quality by studying the impact of mass and heat transfers on reaction kinetics. The approach was that of integrating knowledge in food chemistry, reaction engineering and process engineering to obtain synchronous experimental data on transfers and reactions on three food products (sponge cake, processed cheese and tomato sauce). This served to feed a methodological reflection to complete and make reliable the knowledge of the reaction mechanisms and kinetics, then to formalize and model them in order to optimize the product / process system. This project was founding and structuring for the merger of the UMR SCALE with the UMR GENIAL and the creation of the Calipro team which followed.

I then participated in the **ANR-ALIA Dominove**. In this context I developed the quantitative measurement of furan and supervised the work of a contractual staff (Jessica Malfaire):

Projet ANR–ALIA DOMINOVE (2010-1014)

Title : *Influence of domestic heating on the sensory and nutritional characteristics of pre-fried industrial products*

Funding : ANR (Agence Nationale de la Recherche)

Coordination : B. Broyart (UMR GENIAL)
Parteners : ITERG ; LDC ; McCain ; UMR IAQA ; ANIA ; ACTIA, Lesieur.
My role : contributeur au WP1 sur les développements analytiques (dosage furane)
Summary : The Dominove project aimed to characterize the phenomena of mass and energy transfer during domestic heating (oven, pan) of different industrial products (spring rolls, fries, cordon bleu) and to jointly study the progress of reactions thermo-oxidative degradation of lipids. For this, pilot heating devices have been developed to mimic repeatable and controlled operating conditions. Analytical methods (classic and / or original) have been used to characterize the progress of these reactions. A study on continuous phases and model products was conducted in parallel to help the development and validation of mathematical models relating to transfers and reactions.

My contribution to the **ANR SATIN Project** (2012-2015- Identification of the consequences of the aging of non-stick coatings on baking molds on the chemical and physicochemical characteristics of cereal products such as sandwich loaves), however, was limited to collaboration within the framework of the thesis of L. Huault on the analytical developments related to the dosage of furan.

Currently I participate in the **European project ITN FOODENGINE** This project applies a kinetic multi-response approach to study the change of quality indicators of plant-based food products in relation to the sensory properties and preferences of consumers and finances 13 Marie Curie Sklodowska PhD theses *(www.foodengine.eu)*:

Project Marie Curie Innovative Training Network (ITN-ETN) FOODENGINE (2018-2022)

Title: *Enginomics in food quality design: the case of shelf-stable fruit-, vegetable- and legume-based foods »*

Coordination: KU Leuven (A. Van LOEY)

Partners: KU Leuven (BE), FOOD-UCPH (DK), INRAE (FR)), three large-turnover, multinational, R&D-based food (ingredient) companies (Döhler (DE), Cargill (BE), Unilever (NL)), two medium-sized food (ingredient) companies (GNT (DE), Greenyard Prepared (BE)) and an international market and consumer research company (Haystack (BE))

My role: Contributeur au WP1 (Multi-functional ingredients) dans le cadre du travail de thèse de S. Krause et au WP4 (Skills training) avec l'organisation d'une winterschool en 2021.

Summary : FOODENGINE is a Marie Curie Innovative Training Network (ITN-ETN) for early-stage (ESR) researchers, funded by the European Commission under the Horizon 2020 Programme and has started on January 1, 2018. The objective of FOODENGINE is to train interdisciplinary experts with an intersectoral (from academia to private sector) experience on a beyond state-of-the-art new way of thinking for future food products and food process design, complemented with an extensive transferable skills development.
The consortium of FOODENGINE combines the interdisciplinary expertise and infrastructure of three highly-ranked European Universities/Research institutes with R&D-based food (ingredient) companies into a synergistic consortium to establish an international interdisciplinary and intersectoral pioneering European food training programme.

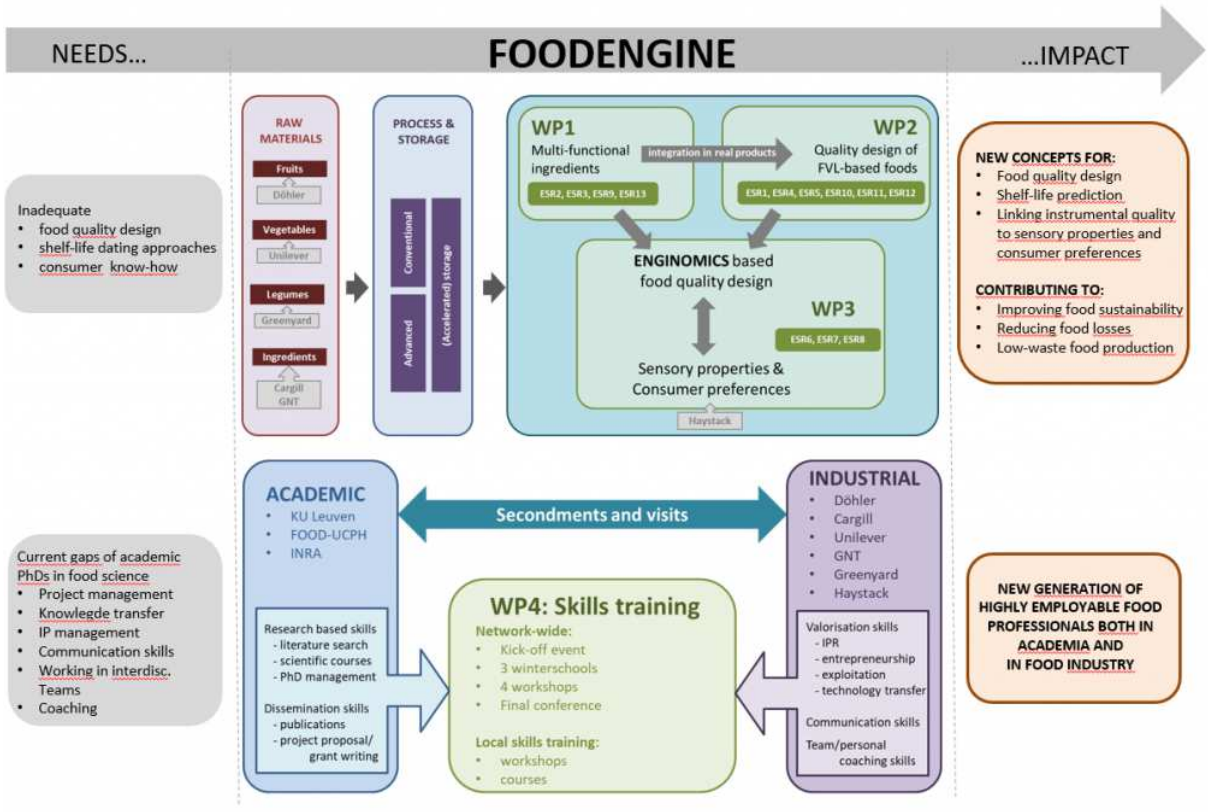

Figure 45: schematic organization of the FoodEngine project

Coordination and management of research and other scientific activities

Since my thesis, I have greatly appreciated participating in collaborative projects and I have always been interested in the aspects of communication and animation.

As part of the FIPDes program, since 2013 I have been coordinating **FIPDes Day, an annual international symposium** on the theme of innovation: "International Talents in Food Innovation and Product Design", in collaboration with 3 European universities (see http: / /www.fipdes.eu/?FIPDes-Day-122). This conference is organized around 5 sessions (Food Design and Engineering, Healthy Food Design, Packaging Design and Logistics, Culinary Innovation and New Product Development, FIPDes Alumni Insights and Perspectives) by inviting renowned international guests ("key note speakers") followed by flash presentations by graduating M2 students. We have set up 3 prizes to encourage scientific and professional communication (prize for the best flash presentation, the best poster and the best photographic representation of the master's thesis work), three poster sessions, networking activities and exchange with industrial partners and Start-Ups hosted by the Food'Inn Lab of AgroParisTech. Around 150 people participate in FIPDes Day each year.

Thanks to the coordination experience of the EMJMD FIPDes, I now know how to work with different actors at the national and international levels and I have developed managerial skills to lead this ambitious program. This international master follows a trajectory of success, with three successive accreditations by the European Executive Agency for Education, Audiovisual and Culture (EACEA), global financial support of around 10M €, a European consortium that works and exciting results as previously illustrated.

Armed with this experience, I took the lead of the Calipro research team (26 staff) for a period of almost two years (2017-2019**), in a pivotal moment** in the preparation of the HCERES report and the merger of two UMR Génial and GMPA which took place on January 1, 2020.

The Calipro team saw the succession of 3 team leaders over the last quadrennial (C. Bonazzi; F. Courtois and then myself) and I therefore took great care and pleasure in preparing and defending the results of the team for HCERES in December 2018. This task allowed me to understand in depth the dynamics of my team and of the UMR Génial as well as in the national and international panorama. I also had the pleasure of reflecting with my counterparts and working in an environment of trust within CoDir.

The process of merging the UMR Génial and GMPA came in a delicate context of successive restructuring and plans to move to the Saclay plateau by 2021. Despite having implemented a highly participative co-construction process new research teams and fostered dialogue with the SPAB department of AgroParisTech for a harmonization of our teaching and research missions, this was quite cumbersome to manage. In this context of change, and as manager of Calipro, I participated in defining the objectives of the new GéPro team (Product Engineering) which was set up on January 1, 2020, the date of creation of the new SayFood “Paris-Saclay Food and Bioproduct Engineering” UMR *(fig. 46)*. Within this team I will co-lead a think tank with my colleague MN Maillard for the definition of research questions at the interface between structuring-reactivity, in order to bring out structuring projects on this thematic. This activity is closely linked to my medium-term research prospects (cf. chapter 5). Figure 46 shows how the questions of matrix-transfer-process interactions, of structuring and chemical reactivity are at the heart of the new UMR, it also shows the 5 multidisciplinary teams newly created following the merger.

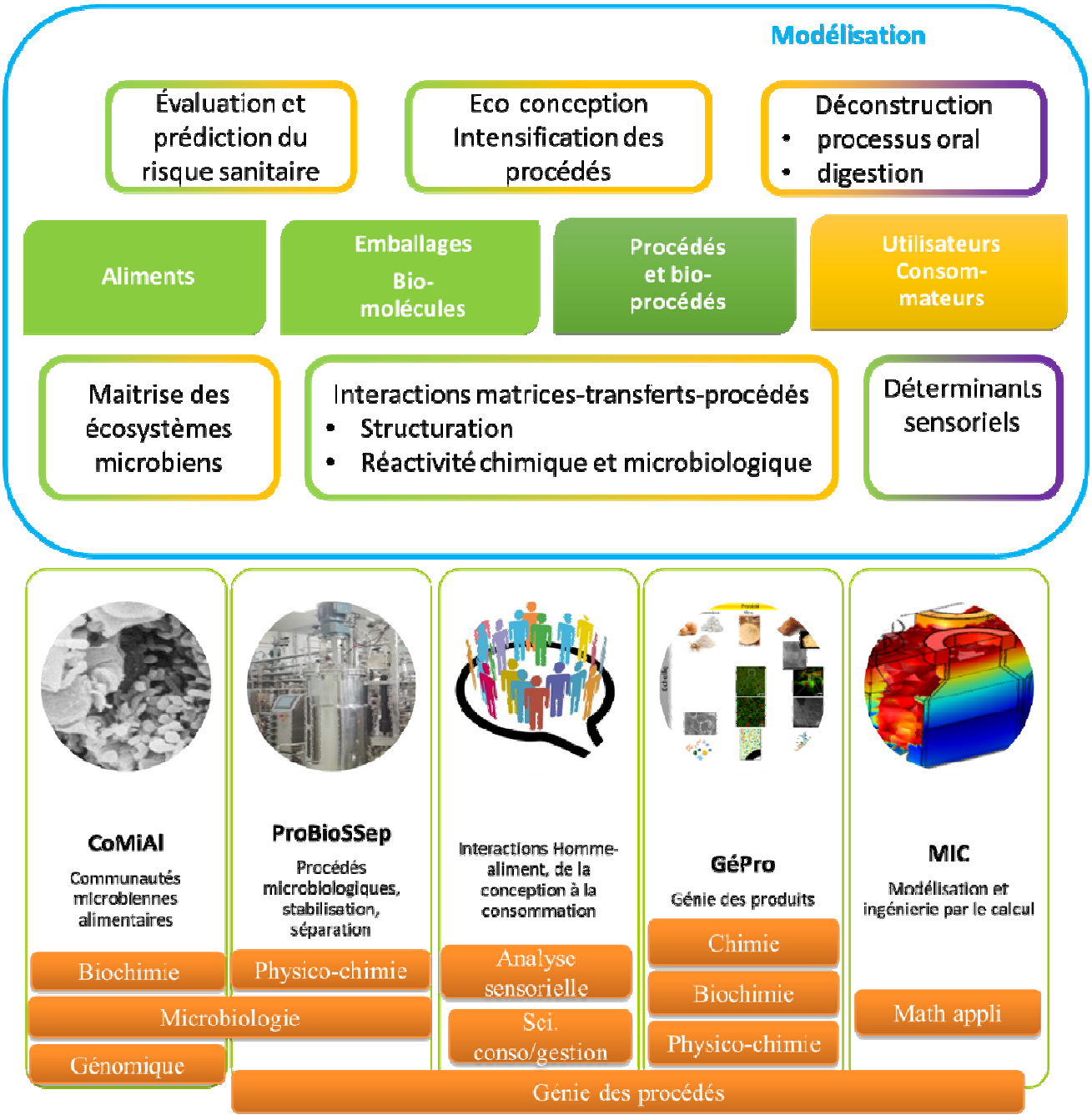

Figure 46: Illustration of the skills perimeter and new teams of the UMR 0782 SayFood. Based on the presentation for the HCERES 2019.

Chapter 5

Prospects & project

Chapter 5 : Prospects & project

The strong point of the research carried out so far has been to identify and follow interesting newly formed compounds for the understanding of the "food system" during its transformation. We have developed an understanding of reactivity in complex products and are able to follow a broad spectrum of volatile and non-volatile markers for prospects of quality control, taking into account the construction of the product and its physical and structural transformations.

This research has contributed to advancing knowledge on the reactivity of food products. However, at global level, **a key element is still under-explored and deserves for me a particular attention for its potential impact on the reasoned conception of food:** it is the relation between food matrix, reactivity and bioavailability of newly formed compounds.

In the current period, increasing attention is paid to sustainable production and consumption on the one hand, and to (ultra)-processed foods and their impacts on health (Fiolet, Srour, Sellem, Kesse-Guyo, Alles, Mejean, and al., 2018, Fardet & Rock, 2019), on the other hand. The intensification of media information have a significant effect on consumers with regard to these products (perception, consumption habits). The negative perception of so-called "ultra-processed" foods and the encouragement by public policies to explicitly reduce the consumption of ultra-processed products[3] (eg a reduction of 20% is currently recommended by the French government[4]), are a very powerful lever for agrifood innovation, with the implementation of large-scale reformulation strategies in order to quickly replace poorly perceived / rated ingredients and / or additives with well-accepted or promising alternatives. An interesting example is the rapid evolution towards the use of emerging ingredients (e.g. less refined ingredients, vegetable protein sources, functional ingredients, natural substitutes for additives) or towards the simplification of technological itineraries, with the aim of promoting natural raw materials with a nutritional connotation positively perceived and include them in a sustainable production approach (think of legumes).

In this very dynamic context of food innovation linked to health and sustainability issues, I ask myself the following questions:

1) What is the impact of emerging ingredients identified as "natural" on the generation of newly formed compounds in processed products?

2) What is the relationship between food matrix, transformation and bioaccessibility of newly formed compounds?

3) Can this relationship influence microbiota-human interactions (and how could we manage it)?

So I want to **focus on two distinct and yet interconnected aspects** to understand responsiveness and holistically control the quality of food.

[3] Au même temps, la communauté scientifique explore le sens de la définition d'aliment « ultra transformé », avec un échange dialectique intéressant et passionné, et analyse la pertinence des nouvelles classifications telle que la classification Nova, avec l'idée de clarifier et mieux identifier les différents enjeux sous-entendus, au-delà des enjeux de santé et des enjeux industriels

[4] https://solidarites-sante.gouv.fr/IMG/pdf/pnns4_2019-2023.pdf

Understand the relationships between responsiveness and structure of the food developed to manage quality

I wish to further explore the relationships between food reactivity and structure. I aim to continue to combine targeted and non-targeted approaches via studies in model and real products, in order to understand the reactivity of ingredients (ubiquitous and new ones). The ultimate goal is to manage quality in a holistic way, taking into account functionality, palatability and healthiness of food ingredients, as well as the new applications for which these ingredients are intended.

Structure / reactivity interactions have been identified as a promising subject for the new GéPro team and the study of model products remains a very original approach to pursue for scope. It is indeed possible to modulate the structure of a model product without adding other ingredients / additives but only thanks to the manufacturing process. Indeed, an increasing interest is devoted to the understanding of how thermomechanical processes can modulate the functionality, and therefore the structure, of a product, for an advanced exploitation of the potential of the ingredients and without additional addition of additives. To understand the impact of the structure at different scales (-from macro to micro-) on reactivity, it will therefore be possible to compare the kinetics and the generation profiles of CNF obtained in products with different levels of structure but constant chemical composition, paying attention to measure the mobility of reactants. These results could be compared to those obtained in an aqueous system under the same experimental conditions ([reactants], T, initial pH), thanks to the use of an instrumented reactor available in our laboratory.

Deepen the knowledge on the reactivity of ubiquitous ingredients through the complexification of model products

The methodological study of food reactivity in model products which was presented in *axis III* opens very interesting prospects in the short and medium term, notably thanks to the complexification of the chemical composition of these models as well as to the modulation of their structure. It would be interesting to mobilize the expertise of our laboratory on the analysis and reactivity of antioxidant compounds and lipoxidation products to explore the eventual interaction pathways. The expertise acquired during these years on different model products will be very precious.

The latest thesis work by Jeehyun Lee offers interesting short terms perspectives:

The **introduction of different precursors into model products** would make it possible to test the reactivity of a series of ubiquitous ingredients in solid/semisolid systems. For example, it would be interesting to compare the reactivity of different monosaccharides and in particular that of **fructose**, by comparing the rate of formation and degradation of key intermediates such as dicarbonyl compounds which are key intermediaries in the Maillard and Caramelization reactions. Indeed, the literature on solid simplified systems is very tenuous but the isomerization between fructose and glucose is described as a key step for the formation of deoxyosones in systems with low humidity levels (Kocadagli & Gokmen, 2016). In fructose-based models, it would also be interesting to study the formation and stability of fructose dianhydrides (DAF) which recently revealed interesting prebiotic properties (Cerda, Thammavong, Caqueret, Porte, Mabille, Fernandez, et al., 2018). Similarly, the exploration of the reactivity of other free amino acids such as sulfur amino acids or lysine as well as that of more complex precursors (peptides, oligosaccharides) or the presence of catalysts / co-factors / inhibitors (metals, polyphenols) would allow us to investigate the potential for the formation of compounds of interest (aromas, newly formed contaminants, brown compounds) in simplified products mimicking solid products of plant origin. For example, recently Troise, Wiltafsky, Fogliano, & Vitaglione (2018) have shown that the reactivity of free amino acids in soy products is well correlated with the level of production of protein-bound Amadori compounds. Another study, Hamzalioglu & Gokmen (2018) explored the kinetics of adduct formation between HMF and free amino acids such as lysine and cysteine in order to propose a mitigation pathway for HMF. These studies in model products will allow us on the one hand the acquisition of new kinetic data and on the other hand the identification of reaction products (intermediates, final) resulting from the more or less elaborate combinations of precursors, always in controlled conditions

of transformation. For this second aspect, **a non-targeted approach** is to be implemented, based on the laboratory's expertise on the analysis of non-volatile compounds (UHPLC / QToF-MS, Fluorimetry) and thanks to external collaborations to be built for the further analysis of volatile and non-volatile compounds (e.g. chemometrics, volatolomic approach by GCxGC / ToF-MS, analytical expertise on glycation products). At the moment, a collaboration with Jihène Bouhlel (IR recently recruited in the UMR) has been set up for the chemometric processing of volatile compounds, which will allow us to compare the performance of different methods including the "Paradise" mass extraction and deconvolution algorithm for mass spectra developed by colleagues from the Danish Department of Food Science at the University of Copenhagen (Johnsen, Skou, Khakimov, & Bro, 2017).

Explore the reactive potential of new ingredients / new applications

The ingredients derived from legumes (pulses) have recently been used more and more in the reformulation or design of various processed products with the aim of diversifying the supply of legume-based products, fortifying proteins, optimizing the nutritional profile or substituting wheat / milk / soy ingredients (Sozer, Holopainen-Mantila, & Poutanen, 2017).

The functional properties of these ingredients such as foaming, emulsifying, gelling properties or the nutritional profile are widely studied (Chao & Aluko, 2018; Tiwari, Gowen, & McKenna, 2011; Foschia, Horstmann, Arendt, & Zannini, 2017). The impact of reformulation on the nutritional profile, texture and appreciation of products is the main focus of recent literature (Laleg, Barron, Cordelle, Schlich, Walrand, & Micard, 2017). On the other hand, the potential to form potentially toxic or odorous newly formed compounds in the case of new formulas and processed products is and an area still to be explored and it must raise our interest because of the reactive potential of the mixture of ingredients and the processes used. Indeed, very recently Mesias, Delgado-Andrade, & Morales, (2019) have shown that in new recipes for snacks based on plant sources, greater quantities of HMF, furfural are present compared to classic recipes (up to 3 times higher). In addition, lipid oxidation (enzymatic and autoxidation) is increased in this type of ingredient by the significant presence of PUFA and the activity of oxidative enzymes (lipoxygenases) derived from raw materials. If there is a very abundant literature on "off-odors" derived from the ingredients themselves linked to the source and to their mode of production (Murat, Bard, Dhalleine, & Cayot, 2013; Ma, Boye, Azarnia, & Simpson, 2016), the generation / degradation of specific odoractive compounds in formulated and transformed products is little explored.

To contribute to bringing knowledge on these questions, I recently initiated a new international collaboration within the framework of the **European project ITN FOODENGINE (2018-2022) "Enginomics in food quality design: the case of shelf-stable fruit-, vegetable - and vegetable-based foods ".** This project applies a multi-response kinetic approach to study the change in quality indicators of plant-based food products in relation to sensory properties and consumer preferences and funds 13 Marie Curie Sklodowska theses (www.foodengine.eu).

Thanks to **Svenja Krause's PhD thesis** (Evaluation of the use of vegetable-based ingredients in processed plant-based products, *tab. 2*), recently started, we will explore the potential of ingredients from legumes in a given application. Using a formulation engineering approach, we will study the **reactivity of new pea ingredients (flour, protein isolates, starches)** and the impact of formulation and process parameters (as well as their interactions) on the development of odoractive and / or potentially toxic compounds. Thanks to a **new collaboration with KU Leuven and Cargill** we will be able to include in our study an additional dimension of quality: the nutritional quality of these new recipes (**digestibility of proteins and starch**) **in connection with macro- and microstructure** and properties of the constituents, with a view to multi-criteria evaluation of the determinants of quality for a given application.

With this type of product, we will have a system of choice to investigate the **interactions between Maillard reactions and lipid oxidation** and see how the interactions between process and formulation can modulate the profile of compounds of interest.

Understand the links between reactivity, structure and bioaccessibility of newly formed compounds and explore their impact on microbiota-healthy human interactions

We are beginning to see the immense potential of the symbiosis between our organism and its commensals, of its fragility too (Canani, Paparo, Nocerino, Di Scala, Della Gatta, Maddalena, et al., 2019). If humans evolve very slowly, our commensals adapt / are selected very quickly in response to the diet and can modify the chemical signals sent to their host accordingly. These changes can be reversible during the same generation (Zinöker & Lindseth, 2018). After thousands of years of diet stability, our diet has undergone profound changes in a few decades with the advent of the so-called "Western" diet (diversification, meaty diets, new ingredients, reduced fiber, "soft" structures, and exposure to many exogenous and endogenous molecules…). However, we are just starting to measure the impact of these changes on human-microbiota interactions (Tuohy, Hinton, Davies, Crabbe, Gibson, & Ames, 2006, van Boekel, Fogliano, Pellegrini, Stanton, Scholz, Lalljie, et al., 2010; Zinöker & Lindseth 2018, Monteiro, Moubarac, Cannon, Ng, & Popkin, 2013, Costa, Del-Ponte, Assuncao, & Santos, 2018). On the other hand, the risk assessment linked to dietary exposure to newly formed compounds does not take into account for the moment the impact of these compounds on the commensal / human axis. What is the nature of such an interaction? Could we arrive at new advances in terms of risk assessment, thanks to a new integrated, ecological and dynamic vision of the impact of microbiota on health? This is currently being explored for other types of chemical contaminants (Defois, Ratel, Garrait, Denis, Le Goff, Talvas, et al., 2018).

I find this new perspective in food science absolutely fascinating: to consider / develop / optimize the food most likely to maintain a harmonious symbiosis for our supra-organism (Ercolini & Fogliano, 2018) and I would therefore like to contribute at my level, by bringing my expertise in formulation engineering and reactivity.

I therefore ask myself the question of **how the presence of newly formed compounds in complex and elaborate matrices could influence microbiota-human interactions (and therefore how could we control them).**

There is a wealth of literature on the possible influence on health of Maillard reaction products (PRM) and the in vivo fate of certain target compounds such as advanced glycation products (AGE) (Liang, Chen, Li, Li , & Yang; Zhao, Sheng, Wu, Li, Xu, Nian, et al., 2019). However, recent reviews highlight the need to develop knowledge on the modulation of the intestinal microbiota due to PRM and their metabolites (Aljahdali & Carbonero, 2019; Snelson & Coughlan, 2019).

There is, in fact, a growing interest in the effect of PRM on the microbiota (modulation of the profile of bacteria, generation of compounds with positive impact such as short-chain fatty acids, etc.), with studies focusing mainly on target AGEs such as CML; FL; Pyrraline, (Hellwig, Bunzel, Huch, Franz, Kulling, & Henle, 2015) or more recently on melanoidins (N. Aljahdali, Gadonna-Widehem, Anton, & Carbonero, 2020; Helou, Denis, Spatz, Marier, Rame, Alric, et al., 2015). In parallel, some studies look at the overall effect of processed food products on the microbiota without exhaustively characterizing the molecular factors of such interactions (Delgado-Andrade, de la Cueva, Peinado, Rufian-Henares, Navarro, & Rubio, 2017; Perez-Burillo, Pastoriza, Jimenez-Hernandez, D'Auria, Francino, & Rufian-Henares, 2018).

However, the limited number of these studies and the diversity of the systems investigated make conclusions difficult. The results are indeed often contradictory, which has in particular been attributed to the formation of **very different compounds during the heat treatments** applied to food and which have not been taken into account, until now, in their heterogeneity and comprehensiveness, which requires further clarification (Snelson & Coughlan, 2019; Zinocker & Lindseth, 2018). Furthermore, to my knowledge, there are very few studies on the understanding between digestion of the transformed matrix (taking into account its structure, its composition, and the various reaction products), bioaccessibility of MRP and possible interaction with the microbiota.

Thanks to new in vitro digestion approaches such as the Infogest protocol (Bohn, Carriere, Day, Deglaire, Egger, Freitas, et al., 2018; Mulet-Cabero, Egger, Portmann, Menard, Marze, Minekus, et al., 2020), the interaction between composition and structure has been taken into account recently in studies on the bioavailability of macro- and micronutrients or even of certain contaminants, (Cardoso, Afonso, Lourenco, Costa, & Nunes 2015; Dupont, Le Feunteun, Marze, & Souchon, 2018; Hiolle, Lechevalier, Floury, Boulier-Monthean, Prioul, Dupont, et al., 2020; Mat, Souchon, Michon, & Le Feunteun, 2020).

I would like to apply this approach to **investigate the fate of newly formed products (especially those with low molecular weight) as a function of the structure of the food matrix and the consequent impact on the microbiota / host interactions.** The creation **of the new SayFood Unit Research Unit will indeed open the doors to new collaboration opportunities** and allow us to bring together our skills in formulation engineering, chemical reactivity, construction / deconstruction of food.

To carry out this project, I plan **to set up a collaboration with the Probihôte team of Micalis** (France) which studies the commensal / host interactions by in vitro and in vivo methods and with my colleagues from Grignon who have developed a dynamic in vitro digester mimicking the stomach and intestinal stages of digestion and whose functioning has been validated in comparison with in vivo tests (Didgi®). Up to now, the first discussions with the Probihôte team are ongoing for a collaboration that could be set up at the beginning of 2021, according to terms that remain to be defined.

I see a first project in 3 main stages: first with the exploration of the bioaccessibility of the newly formed compounds (NFC) from matrices with different structures but with controlled composition and reactions, via the Didgi® in vitro digester system. Then a fermenter study to assess the effect of bioavailable NFC on the microbiota, and a final phase of in vivo assessment to highlight the structure / composition / NFC relationships on the microbiota response. Some elements are indicated in the diagram of **figure 47**. To start such a project I would like, at first, to focus on furanic and the Strecker's compounds, then extend to more complex mixtures, in collaboration with the French teams working in glycation and melanoidins (polymers containing both furan nuclei and Strecker products) and teams working in metabolomic and chemometric analyses. In the longer term, international collaborations could be set up as part of a larger project, in particular with the Food Biochemistry laboratory and the Microbiome Task Force of the University of Naples and the Food Quality Design-WUR department, to go further in a reverse engineering approach taking into account the dimensions of sensory pleasure, nutrition and well-being.

Figure 47: Project brief on the bioavailability of NFC in transformed food and impact on microbiote/host interaction.

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Chapter 6 :

Scientific Production

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Oral11. **Rega B.**: « Un jus d'orange bien frais… » (**2003**). Forum des Jeunes Chercheurs, 12-13 Juin, Dijon, France. *Prix pour la meilleure communication orale (session 3).*

Oral12. **Rega B**., Guichard E. (**2003**). « La perception du frais dans les jus d'orange ». Le frais en aromatique, Club Arômes alimentaires ECRIN-Recherche-Enterprise; 6 Juin, Ecole Nationale du Génie Rural des Eaux et Forêts, Paris, France.

Invited conferences

C-INV1. **Rega B.** (**2019**). "Model cakes help us understanding food reactivity leading to food quality determinants". 9th International Workshop on Molecular and Physical Gastronomy: Flavour trough cooking. 4-7th June 2019, Paris, France.

C-INV2. **Rega B.** (**2018**)**.** « Réaction de MAILLARD dans les aliments transformés : produits modèles et modèles de produits pour comprendre, prédire et optimiser les différentes dimensions de la qualité ». Colloque du comité d'experts francophones sur la glycation et la réaction de Maillard (FMARS)8th October, 2018, Beauvais, France.

C-INV3. **Rega B.** (**2018**)**.** *"How to strengthen contact with relevant stakeholders, expecially in the labour market".* General Prodejip Conference, 26th October 2018. Brussels, Belgium.

C-INV4. **Rega B.** (**2018**). *« L'offre de formation dans l'enseignement supérieur en Europe », le cas de l'Erasmus Mundus FIPDes. Table ronde.* 14èmes Rencontres F. Rabelais, Cuisines d'Europe Cuisines Europeennes. 8-9 decembre 2018, Tours, France.

C-INV5. **Rega B.** (**2018**). The Erasmus Mundus FIPDes: an example of successful European joint programme for food innovation and product design. FICHAT Network, Ambassade de France en Irlande, 1st March 2018, Dublin, Ireland.

C-INV6. **Rega B.** (**2018**). Journée Erasmus de l'Université Paris Saclay UPSAY, animation d'un atelier sur le partage des bonnes pratiques, 12 oct 2018, Institut d'Optique, Saclay, France.

C-INV7. **Rega B.** (**2017**). EMJMD Cluster meeting – EACEA, Table ronde: *"How to work forward the sustainability of EMJMD"*, 26-28th June, 2017, Brussels, Belgium.

C-INV8. **Rega B.** (**2017**)**.** Monter et réussir un master conjoint, FIPDes comme étude de cas. Le point de vue de la coordinatrice. Journées d'information Erasmus+ « Enseignement supérieur » de l'Agence Nationale Erasmus 2E2F. 28 Septembre, Nantes, France.

Educational Books and Tools

OP1. **Qualité et sécurité sanitaire des aliments (Ressource électronique)** (2006), Coord. C. Wegscheider ; resp. O. Cerf. **B. Rega**; interv., M.N. Bellon-Fontaine, **B.Rega**, F.H. Bolnot, O. Cerf, et al. Série *Alimentation & nutrition humaines*, 6 DVD-R. Editions Éducagri.

Graduate theses and dissertations

D1. **Rega B.** (**2003**) « Texture-flavour interactions : how physicochemistry explains sensory perception in orange juice ». Doctoral Thesis, Université de Bourgogne et Università di Napoli « Federico II », (lingue anglaise).

D2. **Rega B.** (**1998**) « Studio delle modificazioni strutturali delle sieroproteine di latte sottoposto a trattamenti termici ». Tesi di Laurea (mémoire de Master 2), Università di Napoli « Federico II », (lingue italienne).

Works supervised by the author

Co-supervised PhD theses

Th1. **Fehaili S. (2010)** : Développement d'un simulateur de cuisson pour l'étude du couplage entre les transferts d'énergie et de matière et les cinétiques de réactions de Maillard ayant lieu au cours de la cuisson de produits céréaliers de type génoise. Doctorat en Sciences et Procédés Alimentaires, AgroParisTech, Massy, France.

Th2. **Deterre S. (2012)** : Compréhension des mécanismes physicochimiques ayant lieu lors de la production d'un distillat d'orange. Rôle des différentes étapes d'élaboration sur la qualité chimique et organoleptique du produit fini. Doctorat en Sciences et Procédés Alimentaires, AgroParisTech, Massy, France.

Th3. **Bousquières J. (2017) :** Impact de la composition et des procédés sur la réactivité d'un produit modèle alvéolé. Doctorat en Sciences et Procédés Alimentaires, AgroParisTech, Massy, France.

Th4. **Cepeda Vasquez M. (2017) :** Rôle des ingrédients et des précurseurs réactionnels sur la génération de marqueurs moléculaires liés à la qualité sanitaire et sensorielle d'un produit céréalier de type cake. Doctorat en Sciences et Procédés Alimentaires, AgroParisTech, Massy, France.

Th5. **Lee J. (2019):** Analyse et modélisation de la réactivité au cours de la cuisson d'un produit modèle mimétique d'un produit céréalier type génoise. Soutenance prévue en 2019. Doctorat en Sciences et Procédés Alimentaires, AgroParisTech, Massy, France.

Master and engineer internship dissertations

Mast1. **Narainsamy, K. (2004):** Etude de faisabilité pour l'extraction en ligne d'un procédé de cuisson. Mémoire de stage de 1ère année, Magistère de chimie de l'Université Paris Sud. 22 pag.

Mast2. **Haouache, M. (2005):** Evaluation physico-chimique et validation sensorielle d'extraits aromatiques de cuisson. Mémoire de diplôme d'ingénieur ENSIA, 22 pag.

Mast3. **Joelitiana, S. (2005):** Analyse d'arômes générés au cours de la cuisson d'un élément modèle de génoise. Master 1ère année en Chimie fondamentale et appliquée, Université Paris VI, 16 pag.

Mast4. **Morales, A. (2006):** Etude de la formation de composés volatils lors de la cuisson de produits céréaliers. Master 2ème année en Sciences et Technologies du Vivant et de l'Environnement, mention « Aliments et Bio-produits », AgroParisTech, Massy, France. 20 pag.

Mast5. **Maire, M. (2007):** Influence de la formulation (et des procédés) sur la génération des composés volatils dans les produits céréaliers. Mémoire probatoire en Science de la vie, Option Biochimie industrielle et agro-alimentaire, CNAM, 77 pag.

Mast6. **Machado, E. (2007):** Etude des relations entre degré de cuisson et acceptabilité sensorielle d'un produit céréalier type génoise. Master 1ère année en Sciences et Technologies du Vivant et de l'Environnement, mention « Aliments et Bio-produits », AgroParisTech, Massy, France. 20 pag.

Mast7. **Machado, E. (2008)**: Effet de la nature des oses sur la cinétique de la réaction de Maillard dans un produit céréalier modèle type génoise. Master 2ème année en Sciences et Technologies du Vivant et de l'Environnement, mention « Aliments et Bio-produits », AgroParisTech, Massy, France. 20 pag.

Mast8. **Maire, M. (2009):** Impact de la composition en matières grasses sur les arômes générés au cours de la cuisson d'un aliment modèle type génoise. Mémoire de diplôme d'ingénieur CNAM en Science de la vie, Option Biochimie industrielle et agro-alimentaire, 227 pag.

Mast9. **Hanaei, F. (2010):** Etude de l'impact de l'oxydation des lipides sur le développement du potentiel odorant d'un produit céréalier modèle en cours de cuisson. M2 en Sciences et Technologies du

Vivant et de l'Environnement, mention « Aliments et Bio-produits », AgroParisTech, Massy, France. 20 pag.

Mast10. **Boukhari, S. (2011):** Evaluation de la qualité d'une génoise emballé dans une barquette biodégradable. M1 en Sciences et Technologies du Vivant et de l'Environnement, mention « Aliments et Bio-produits », AgroParisTech, Massy, France. 20 pag.

Mast11. **Claire, S. (2012):** Suivi de la formation et libération du furane, contaminant généré lors de la cuisson ménagère de produits frits. M1 en Sciences et Technologies du Vivant et de l'Environnement, mention « Aliments et Bio-produits », AgroParisTech, Massy, France. 20 pag.

Mast12. **Gonzales Jordan, A. (2013):** Formulation and caracterisation of an eggless gluten free sponge cake model for mastering the structure and reactivity of its constituents. M2 Erasmus Mundus Master in Food Innovation and Product Design, AgroParisTech, Massy, France. 20 pag.

Mast13. **Srivastava, R. (2016):** Generation of furanic compounds in model sponge cakes with respect to changes in formulation and baking conditions. M2 Erasmus Mundus Master in Food Innovation and Product Design, AgroParisTech, Massy, France. 20 pag.

Annexes

Annex 1 : Selection of articles in chronological order of publication

Annex 2 : Summaries of PhD thesis projects (finished)

Annex 3 : Organizational charts of UMR Genial and SayFood

Annex 4 : Network of the main collaborations established through national and international research projects

Annex 5 : Supervision of research activities at master's level

Annex 6 : FIPDes Mission

Annex 7 : Summary sheet of teaching activities