LOQ 1a: Lipid Oxidation Fundamentals

Chairs: Fereidoon Shahidi, Memorial University of Newfoundland, Canada; and Weerasinghe Indrasena, DSM Nutritional Products, Canada

Role of Antioxidants and Stability of Frying Oils
S.P.J. Namal Senanayake*, *Camlin Fine Sciences, USA*

The role of antioxidants in delaying lipid oxidation of edible oils and fats is well known. Synthetic antioxidants are often added to edible oils and fats to retard oxidation during storage and frying; however, consumer reaction on synthetic antioxidants remains undesirable. Consequently, there is an increasing interest in the search for naturally-derived antioxidants for frying applications. The analysis of the different methodologies for frying oils include the peroxide value, anisidine value, free fatty acid content, Oil Stability Index (OSI), viscosity, and residual antioxidant levels, among others. In this presentation, the chemistry of frying as well as action and fate of antioxidants during frying will be discussed. Several analytical assays will be employed to compare the performance of natural antioxidants against synthetic antioxidants during frying. In addition, an overview of the literature on natural antioxidants and their performance under frying conditions will be presented.

Impact of Oxidized Proteins and Lipids and Suppression of Atherosclerosis Development by Functional Food Bioactives and Their Metabolites
Jack N. Losso*, *Louisiana State University, USA*

Atherosclerotic cardiovascular disease accounts for about 30% of global deaths and is the principal contributing factor to cardiovascular-related global mortalities. Atherosclerosis-associated-death is still on the rise and expected to more than double by 2030. The pathogenesis of atherosclerosis is multifaceted and includes oxidative stress, endothelial dysfunction, insulin resistance, and a large number of inflammatory and immunologic factors. Traditional risk factors for the development of cardiovascular disease complications include smoking, dyslipidemia, hypertension, and diabetes. Therapies mostly associated with cholesterol synthesis inhibition have been developed and directed at these traditional risk factors with major clinical benefits. Yet, a high residual risk of cardiovascular disease development still remains. Dietary modification and physical activity afford modest amount of cholesterol lowering. The role of inflammation and the immune system pathways in the development of atherosclerosis is well established. Oxidized low density lipoprotein-induced activation of macrophages and smooth muscle uptake of lipoprotein and subsequent intimal migration and proliferation play a critical role in the early stages and subsequent progression of atherosclerosis. There is a lack of therapies directly targeting macrophages and smooth muscle cells, largely due to the concern for systemic toxicities. IFN-γ signaling pathways play a significant role in macrophages and smooth muscle cells proliferation and atherosclerosis development and have been identified as promising targets for therapy. The use of prebiotic metabolites to specifically target IFN-γ signaling in macrophages and smooth muscle cell proliferation and

improves the inflammatory and immune system is a novel promising approach that will be discussed.

Antioxidant Evaluation: Why *in vitro* and *in vivo* Results do not Always Correspond? Fereidoon Shahidi*, *Memorial University of Newfoundland, Canada*

The efficacy of antioxidants is often assayed by monitoring their free radical scavenging efficacy, metal ion chelating ability, and reducing power. However, preparation steps prior to determination as well as post consumption variables influence the observed effects and are responsible for differences often make comparison of the results difficult. These factors include, but not limited to, extraction, absorption and metabolism of the bioactives present. As most of the antioxidants used in foods and biological systems are phenolic and polyphenolic in nature, this presentation concentrates on the nature of the starting material in terms of being fresh or dry, particle size and the medium in which they are evaluated as well as their chemical structures. In addition, the nature of the extraction solvent(s), the temperature and the time used are important. Furthermore, phenolic compounds exist in the free, soluble esters and glycosides as well as insoluble-bound forms. Release of the phenolics from cell wall matrices is therefore essential for accurate evaluation and quantitative determination. Once consumed, phenolics are metabolized and efficacy of metabolites might be quite different from those of the starting materials. The absorption of different phenolics may also be quite different, hence simulated digestion and possible use of cell lines might bridge the existing gap between in-vitro and in-vivo evaluation methods. Examples will be provided to shed light on the evaluation of antioxidant efficacy.

Application of Differential Pulse Voltammetry to Determine the Efficiency of Stripping Tocopherols from Commercial Fish Oil Rachele A. Lubeckyj[1], Jill Moser[2], and Matthew Fhaner*[3], *[1]Michigan State University, USA; [2]USDA, ARS, NCAUR, USA; [3]University of Michagan-Flint, USA*

Electrochemical techniques have been used to monitor antioxidant species for many years due to the numerous benefits this methodology has to offer. However, electrochemistry still lags behind other methodology, despite its benefits, for routine laboratory analysis. This work aimed to determine how well electrochemistry, specifically differential pulse voltammetry, could be used to monitor the removal of tocopherols from commercial fish oil compared to established techniques such as high-performance liquid chromatography (HPLC). Commercial fish oil was stripped, and remaining tocopherol species were analyzed using electrochemistry and HPLC. Their relative figures or merit were compared, and it was found that the limits of detection and quantitation were similar between the two techniques. However, electrochemistry analysis proved to be more time efficient and produce less chemical waste per sample analysis compared to HPLC. The potential advantages of electrochemistry have led our group to continue investigation into other research areas in which it can be implemented. This recent work in our research lab, highlights utilizing electrochemistry to monitor the depletion of antioxidants in fish oil during time course studies and will also be briefly introduced.

LOQ 1b: Optimal Application of Antioxidants in Food with Respect to their Protection Mechanism

Chairs: Xin Tian, Kalsec, Inc., USA; and Thanh P. Vu, University of Massachusetts Amherst, USA

The Oxidative Stability of Fish Oil Enriched Cow and Soy Milk and the Effect of Adding Rosemary Extract Xujian Qiu, Charlotte Jacobsen, and Ann-Dorit Moltke Sørensen*, *Technical University of Denmark, Denmark*

There is a growing interest in enriching food with long chain (LC) omega-3 polyunsaturated fatty acids (PUFAs), especially EPA and DHA, due to its health beneficial effects. However, it is challenging to incorporate the PUFAs to food and keep them oxidative stable during shelf life. This is due to the highly susceptibility of these LC PUFAs towards lipid oxidation. One strategy for the food industry is to use antioxidants e.g. natural antioxidants. Rosemary extract is one of the most popular natural antioxidants on the market. The extract contains carnosic acid and carnosol as major components and other minor components which can act as antioxidants. Therefore, the aim of the study was to evaluate the effect of rosemary extract on the oxidative stability of fish oil enriched cow and soy milks. Both peroxide value and volatile secondary lipid oxidation products were determined to monitor the progress of lipid oxidation during storage (12 days, 2°C). Rosemary extract could inhibit the lipid oxidation in the cow milk. Soy milk samples having much higher unsaturated fatty acid content showed better oxidation stability compared to cow milk regardless of the inclusion of rosemary extract or not. The concentration of carnosic acid and carnosol, arrived from the rosemary extract addition, was significantly more reduced in soy milk samples compared to cow milk. Analysis of the bioactive compounds in the fish oil enriched soy milk demonstrated that chlorogenic acid could contribute to the lipid oxidation stability of this product.

Enzymatic Functionalization of Vinyl Phenols and Evaluation of their Resulting Antioxidant Properties in Cell Model Systems Jérpome Lecomte*, Erwann Durand, and Pierre Villeneuve, *CIRAD, France*

Vinyl phenols were lipophilized through the electrophilic addition of peracids to its vinylic double bond. Those peracids were formed in situ, by the Candida antarctica lipase-B-assisted perhydrolysis of carboxylic acids ranging from C2 to C18, in hydrogen peroxide solution. The addition of peracids with 4−8 carbons in their alkyl chains led to the formation of two regioisomers, with the prevalence of hydroxyesters bearing a primary free hydroxyl. This prevalence became more pronounced when peracids with longer alkyl chains (C10−C18) were used. The antioxidant activity of the resulting hydroxyesters was assessed by means of the conjugated autoxidizable triene (CAT) assay, and on cell model systems.

Impact of Modified Lecithin on the Antioxidant Activity of alpha-Tocopherol in Bulk Oils

Eric A. Decker, and Anuj G. Shanbhag*, *University of Massachusetts Amherst, USA*

Lipid oxidation is a challenge faced by the food industry since it causes a decrease in quality and the shelf life of lipid containing foods. In order to delay the oxidation in lipids, food industries make use of artificial antioxidants. However, these antioxidants are chemically synthesized and consumers desire simpler and cleaner labels without artificially synthesized antioxidants. The hypothesis of this study is to the use phospholipids to improve the shelf life of oils rather than using artificial antioxidants. Addition of 1000 microM phosphatidylethanolamine (PE) to stripped soybean oil containing 100 microM of alpha-tocopherol was able to extend the lag phase of the oil compared to tocopherol alone by 10 days. However, PE at the same concentrations acted as a pro-oxidant in oil without tocopherol (lag phase decreased by 2 days compared to control). The reason for the observed synergism could be due to tocopherols being regenerated by PE, which was shown by HPLC. This study also examined the possibility of enzymatically converting PC to PE in egg lecithin. Phospholipase D has transphosphatidylation activity, cleaves one methyl group from PC which is replaced by an amino group coming from ethanolamine. The phospholipids were analyzed by reverse phase HPLC with an evaporative light scattering detector. The lecithin used for the study contained 60% PC and 30 % PE. The lecithin obtained after the enzymatic conversion had 89% PE and negligible PC. The modified lecithin worked synergistically with alpha-tocopherol giving a lag phase extension of 8 days more than tocopherol alone.

Controlling Oxidation in Skin Care Products with Novel Seaweed Antioxidants

Ditte B. Hermund[1], Birgitte R. Thomsen[1], Niruja Sivasubramaniam[2], Shuk Y. Heung[3], Randi Neerup[4], Louise M. Klinder[5], Susan Holdt[2], and Charlotte Jacobsen*[1], *[1]Technical University of Denmark, Denmark; [2]National Food Institute, Technical University of Denmark, Denmark; [3]DTU Food, Denmark; [4]Danish Technological Institute, Denmark; [5]Mellisa Aps, Denmark*

Brown algal extracts are potential functional ingredients in cosmetic formulations (e.g. facial creams), due to their content of a wide range of compounds, such as polyphenolics (phlorotannins), polysaccharides and pigments with both antioxidant and anti-aging activity. Moreover, the antioxidant activity of brown algal extract can increase the oxidative stability of facial cream, and thereby protect functional lipids which are prone to oxidation. Our ongoing work aims to extract highly antioxidative compounds from brown alga, *Fucus vesiculosus* (FV) and *Saccharina latissima* (SL) to explore the application potential for these extracts in facial cream. Water and ethanol extracts were obtained and characterized. The total phenolic content (TPC) and in vitro antioxidant properties were determined along with identification of phenolic compounds, pigments and polysaccharides. Furthermore, antioxidant efficacy, physical and oxidative stability were evaluated by storage trials with facial creams containing extracts (two FV-extracts and three SL-extracts). Results showed that the two algal species had very different antioxidant profiles, e.g. TPC of ethanolic SL-extracts was approximately 150 µg PGE/mL, compared to the

6 times higher TPC in ethanolic FV-extracts. Moreover, the antioxidant properties were highly influenced by extraction media and type of algae. For the F. vesiculosus extracts the high TPC was correlated with high radical scavenging capacity. However, no correlation was observed for the SL extracts, for which the highest TPC was correlated with high metal chelating ability. These results show that SL and FV extracts have bioactivity and applicability to facial creams of interest to the cosmetic industry.

ANA 2c/LOQ 2a: Evaluation and Prediction of Oxidative Stability and Shelf-life

Chairs: Min Hu, DuPont Nutrition & Health, USA; and Richard Della Porta, Frito-Lay, USA

The Combination of High Oleic Oils and Natural Antioxidants as a Powerful Tool for Shelf Life Extension Susan Knowlton*, *DuPont Company, Pioneer, USA*

High oleic oils from soybean, canola, and sunflower have made significant nutritional and stability improvements in food manufacturing as they replace both partially hydrogenated and conventional (high polyunsaturated), commodity oils. Despite their natural stability resulting from a low polyunsaturated fatty acid content, some manufacturers require further improvements in shelf life stability as they replace synthetic antioxidants in their formulations. Traditional antioxidants like TBHQ, BHA, BHT, and others have fallen into disfavor as consumers are demanding shorter, simpler, and more 'natural' ingredients on food packaging labels. The combination of high oleic oils with natural antioxidants is a valuable tool to meet these demands. Data showing the extension of shelf life achieved with these combinations will be presented.

Chickpea Germination Improves the Antioxidative Activity of its Soluble Phenolic Compounds Minwei Xu* and Bingcan Chen, *North Dakota State University, USA*

Soluble bound phenolic compounds (SBPCs) extracted from germinated chickpea (*Cicer aretinium* L.) were fractionated using SEC-HPLC coupled with auto fraction collector regarding to the molecular weight variation. Three fractions categorized by molecular weight were collected at the optimum germination time (6 days). *In vitro* assay, including total phenolic content (TPC), 2', 2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging ability and oxygen radical absorbance capacity (ORAC), and striped soybean oil-in-water emulsion system were employed to evaluate the antioxidative activity of each fraction. LC-QTOF-MS was employed for identifying the structure change of soluble bound moieties which can explain the variation of the antioxidative activity. Molecular weight of SBPCs tended to increase during chickpea germination. Higher molecular weight soluble phenolic compounds had greater antioxidative activity in emulsion system. Some of the structures of SBPCs were identified by LC-QTOF-MS, which may be related to the difference of antioxidative activity in each fraction. The findings can be applied to exploit antioxidants with strong antioxidative efficacy in food systems.

Antioxidant Activities of Sugars and Protein in Low Moisture Cracker System Thanh P. Vu*, Lili He, D. Julian McClements, and Eric A. Decker, *University of Massachusetts Amherst, USA*

In American diet, low moisture foods, such as crackers, are a top saturated fat contributor exposing a potential risk of coronary heart disease for American consumers. Replacing saturated fat by unsaturated fat could improve the nutritional properties of crackers, yet this would require antioxidant strategies to prevent lipid oxidation and maintain the shelf life of the product. In this study, reducing sugars were found to increase oxidative stability in crackers. Glucose, maltose and maltodextrin at the same dextrose equivalence resulted in increased hydroperoxide (30, 48, and 48 days, respectively)

and hexanal lag phases (60, 81, and 78 days, respectively), compared to control cracker (9 day hydroperoxide lag phase and 33 day hexanal lag phase). The antioxidant activity of maltose was effected by water activity (aw) and concentrations. At aw values of 0.22 and 0.68, maltose increased hydroperoxide and hexanal lag phases, compared to its activity at aw 0.05. For example, crackers with 5.4% maltose at aw = 0.22 and 0.68 had 63 day and 186 day hexanal lag phases, respectively, compared to 48 days at aw = 0.05. Gluten addition from 2.5 to 10%, at aw = 0.05, did not affect oxidative stability, but at aw = 0.68 it increased hexanal lag phases. Casein only slightly increased hexanal lag phase at 7.5 and 10%, aw = 0.22. The ability of reducing sugars with low sweetness (e.g. maltose) to inhibit lipid oxidation in model crackers suggests that they could be an effective antioxidant strategy.

Oxidative Stability of Margarines, Shortenings and Spreads Min Hu*, *DuPont Nutrition & Health, USA*

Oxidative stability and shelf life of food emulsions like mayonnaise and salad dressing have been widely studied. However, the oxidative stability of W/O food emulsions such as margarines, shortenings and spreads have not been thoroughly studied yet, and the researches on this area have started drawing a great deal of attention in both industry and academia. Usually, a bulk oil or fat may be more oxidatively stable than an O/W emulsion containing the bulk oil or fat. How about the case when comparing an O/W food emulsion with a W/O food emulsion? Prooxidant transition metal ions like ferrous iron have a big impact on oxidative stability of O/W food emulsions such as mayonnaise and salad dressing. What is the case when a W/O emulsion like a 40% fat spreads contains transition metal ions? An antioxidant working well in a O/W food emulsion would work efficiently in an W/O emulsion? The presentation will highlight different evaluation methods being used to assess the oxidative stability of butter fat, spreads and margarines, investigate the impacts of different antioxidant blends on the oxidative stability of spreads with varying fat contents, and study how chelators could impact the oxidative stability of different spreads containing varying levels of fat.

Shelf-life Extension of Meat and Meat Products by Using Natural Antioxidants Henna F.S. Lu*, *Kalsec Europe Ltd, UK*

Recently, the use of natural antioxidants has gained attention globally as the result of rising consumer demand for clean label solutions. Due to the presence of unsaturated fat in membrane phospholipids, lipid oxidation occurs in meat during processing and storage. Oxidative stability of various meat and meat products including ground beef, British sausage and chicken fillets were conducted. Meat and meat products were prepared with and without inclusion of antioxidants, followed by storage at different temperature and packaging condition. The stability was monitored through measurements such as visual observation, color measurement, sensory evaluation and secondary volatile oxidation profile by GC-MS (SPME). The effect of synthetic antioxidants such as BHA, BHT, Sodium Metabisulphite and ascorbic acids versus natural antioxidants such as rosemary, green tea, vinegar and acerola on the oxidative stability of meat and meat products were investigated. Results showed that inclusion of natural antioxidants significantly improved the shelf life of meat products. A better

color protection, better sensory attributes and a lower level of oxidation compounds were observed in products with antioxidants added. In addition, different secondary volatile oxidation profiles were obtained for different meat products. In short, natural antioxidant showed a similar performance as compared to that of synthetic antioxidant and therefore provide an alternative to replace synthetic antioxidant. The finding of these studies provide valuable information and new insights to meat suppliers to improve the shelf life of their meat and meat products.

Antioxidant Testing – An Application Review.
Rick Della Porta*, *Pepsico/Frito-Lay, USA*

A review of the practices and applications of testing antioxidants on edible oils. The challenge between academic research and practical application is critical for getting a true understanding of how and antioxidant may be used. The test protocols and analysis methods are reviewed in general terms in hope of making a better connection between researchers and end-users.

ANA 2d/LOQ 2b: Sensory Analytics and Analytical Methods for Assessing Lipid Oxidation and Shelf-life

Chairs: Jian Kong, Abbott Nutrition, USA; and Richard Della Porta, Frito-Lay, USA

Antioxidant Efficacy and Impact of Storage Conditions. Marie Shen[1], Lan Ban[1], and Chandra Ankolekar*[2], *[1]Kemin Food Technologies, USA; [2]Kemin Industries Inc., USA*

Oxidative stability of oils can be measured by accelerated studies such as OSI, Schaal oven, or by monitoring real time chemical and sensory changes at ambient condition. Most of the literature have depended on accelerated conditions for evaluating antioxidant efficacy for the relative ease and quick results. However, debates over the reliability and accuracy still exist. And it is not clear whether complex mixture as plant extracts behave the same way as synthetic antioxidants. We hope to answer these questions with full analyses of free radicals, peroxides, secondary oxidative byproducts and active compound degradation in the treated oils that are stored in both accelerated and ambient conditions. In this study, common ingredients including TBHQ, rosemary extract (RE), mixed tocopherols (MT) and oil soluble green tea extract (OSGT) were tested. Comparing one-year ambient storage and 30-day accelerated storage, it is showed that although the absolute values for each test parameter were not the same, the trends in antioxidant efficacy were every similar. For example, OSGT showed strong dose response in both conditions and performed better than RE and MT. However, the relative degrees of improvement varied for RE and OSGT, that under ambient storage, their relative performances were better. This improvement positively correlated with the improved stability of the active compounds under ambient storage condition. Based on this study, we confirmed that accelerated conditions can serve as quick reference tools but it is needed to establish ambient models that both the activity and stability of an active compound would serve as independent parameters.

Sensory Directed Chemical Analysis of Oxidized Marine Oils Roy D. Desrochers*, *Tufts University Sensory and Science Center, USA*

Abstract not available

Developing a Sensory Oxidation Quality Scale Monica L. Godbout*, *Abbott Nutrition, USA*

Abstract not available

Assessing Virgin Olive Oil Stability and Shelf Life at Moderate Conditions by FTIR Spectroscopy Endowed with a Mesh Cell Accessory Noelia Tena[1], Ramón Aparicio-Ruiz[1], Ana Lobo[2], María Teresa Morales[3], Aparicio Ramón[2], and Diego L. García González*[1], *[1]Instituto de la Grasa (CSIC), Spain; [2]Instituto de la Grasa (CSIC); [3]University of Seville, Spain*

Virgin olive oil (VOO) stability is one of the major topics today because producers are demanding more effective methods to guarantee that oils from extra virgin category remains in this high-quality category during all the shelf life. However, moderate conditions of light and temperature are sometimes enough to produce a quality loss in a few months. The current methods (e.g., Rancimat) apply high temperatures and, therefore, their results are hardly correlated with the real conditions of

storage. In this context, mesh cell has been proposed as a rapid tool designed to monitor chemical changes that occur as a consequence of oxidation at moderate conditions by Fourier transform infrared (FTIR) spectroscopy. In order to evaluate this approach, monocultivar VOOs have been stored in mesh cells under different temperatures (at 23, 35, 65°C) and different light intensities (400, 1000, 7000 lx) simulating the real conditions during storage and transport. The oil stability of the samples determined by using this accessory has been compared with the oil stability determined with Rancimat. The FTIR spectra revealed a remarkable increase of hydroperoxides and the subsequent formation of secondary oxidation products (e.g., alcohols). The fact that this method measures the stability of the oil from a multi-factor perspective (temperature and light) and includes several chemical species (primary and secondary oxidation products) makes the results more reliable to optimize VOO handling (e.g., packaging and storage temperature) according to the real conditions of storage.

LOQ 3a/PRO 3.2a: Effect of New Processing Technologies on Lipid Oxidation

Chairs: David Johnson, Kalsec Inc., USA; and Antonios Papastergiadis, Desmet Ballestra, Belgium

Oxidative Stability of Tomato-based Matrices Enriched with n-3-LC-PUFA Derived from Microalgae Lore Gheysen[1], Nele Lagae[1], Jolien Devaere[2], Koen Goiris[4], Luc De Cooman[2], and Imogen Foubert[1], *[1]Katholieke Universiteit Leuven Kulak, Belgium; [2]Katholieke Universiteit Leuven, Technology Campus Ghent, Belgium*

There is a need for an alternative source of n-3-LC-PUFA due to the reducing fish stock. Microalgae could provide such an alternative. In addition, the daily intake of n-3-LC-PUFA is not reached in Western countries. Therefore, it is useful to enrich food products with n-3-LC-PUFA from microalgae. Fruit and vegetable-based products could be valuable matrices to enrich with n-3-LC-PUFA, since they are important carriers of nutrients and fibers and essential in a healthy diet. This study investigates the impact of processing on tomato-based matrices enriched with the microalga Nannochloropsis compared to commercial fish oil. Intact biomass, disrupted biomass and extracted oil were screened as different delivery systems of Nannochloropsis. For each delivery system of Nannochloropsis as well as for commercial fish oil, a tomato-based matrix was made containing 80 mg n-3-LC-PUFA/100 g suspension. The impact of high pressure homogenization, pasteurization and sterilization on the n-3-LC-PUFA enriched matrices was followed in a dual way. First, the matrices were characterized before and after each (mechanical and thermal) process step for their amount of n-3-LC-PUFA, free fatty acids, carotenoids, polyphenols, vitamin C and tocopherols. In addition, all the samples were stored for 12 weeks at 37 °C to follow up their oxidative stability at different time intervals (0, 2, 4, 8 and 12 weeks). The results showed a limited impact of processing and an influence of delivery system. In this study, promising results for the use of microalgal biomass in tomato-based products as an alternative source of n-3 LC-PUFA were observed.

Oxidation and Hydrolysis of Lipids in Marine Edible Shellfishes During Hot Drying Process Dayong Zhou*[1], Zhongyuan Liu[2], Kaiqi Gang[3], Fereidoon Shahidi[4], and Tong Wang[5], *[1]Dalian Polytechnic University, China; [2]College of Food Science & Technology, Dalian Polytechnic University, China; [3]School of Food Science and Technology, Dalian Polytechnic University, China; [4]Memorial University of Newfoundland, Canada; [5]Iowa State University, USA*

Objective: Hot air drying techniques are widely utilized to decrease the water activity and extend the shelf-life of shellfish. So far, little information is available about the impact of the drying process on the lipids in shellfish in which the n-3 LC-PUFA are present primarily as phospholipid. Therefore, the objective of the present study was to evaluate the hydrolysis and oxidation of lipids in marine edible shellfishes such as clams and whelks upon hot air drying.

Methods used: Marine shellfishes were processed by hot air drying, and the lipid content, lipid classes, PL classes, fatty acid composition, acid value (AV), peroxide value (POV), thiobarbituric acid-reactive substances (TBARS)

and total oxidation (TOTOX) value were determined. Furthermore, oxidation (OXITEST) method was used to evaluate the oxidation level and stability of the dried shellfish.

Results: The drying processing reduced percentages of triacylglycerols, phosphatidylcholine and phosphatidylserine but increased percentages of lysophosphatidylcholine and lysophosphatidylethanolamine, indicating the hydrolysis of the lipids. Interestingly, the POV, TBARS and TOTOX all decreased after the hot air drying process. However, the significant decline of the induction period for the dried shellfish at elevated temperatures indicated their higher oxidation level, poor oxidative stability and reduction of shelf-life.

Conclusion: The traditional oxidation measurements, such as AV, POV, TBARS even TOTOX are inadequate for evaluating the level of lipid oxidation in shellfish upon hot air drying process. In contrast, OXITEST method is shown to be an effective tool for estimating lipid oxidation level for hot air dried shellfish.

Effect of Spray-Dried Flavonoid Microparticles on Oxidative Stability of Methyl Linoleate as Lipid Model System Manuel J. Palma[1], Gloria Márquez-Ruiz[2], Paula García [3], Francisca Holgado[4], Cristina Vergara [3], Begoña Giménez[5], and Paz S. Robert[6], *[1]Universidad de Chile, Chile; [2]Instituto de Ciencia y Tecnología de Alimentos y Nutrición (ICTAN-CSIC), Spain; [3]Departamento de Ciencia de los Alimentos y Tecnología Química, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Chile; [4]Instituto de Ciencia y Tecnología de Alimentos y Nutrición (ICTAN-CSIC); [5]Departamento de Ciencia y Tecnología de los Alimentos, Facultad Tecnológica, Universidad de Santiago de Chile, Chile; [6]Universidad de Chile, Chile*

The objective of this work was to evaluate the antioxidant action of microencapsulated flavonoids with specific differences in chemical structure, namely, quercetin (Q) and epicatechin (E) in bulk methyl linoleate (ML) under oxidation conditions at 60ºC, in a Rancimat apparatus. Microencapsulated Q and E were prepared by spray-drying using inulin (IN) as encapsulating agent (Q–IN and E–IN) as well as with Capsul (C) as channelizing agent (Q–IN–C and E–IN–C). Microparticles were added to ML and results showed that Q microparticles markedly improved its oxidative stability by increasing the induction period values and delaying the formation of oxidation compounds, as determined by high-performance size-exclusion chromatography, with respect to E microparticles, thus suggesting the importance of flavonoid C-ring substitution. Remaining levels of Q in the lipid system throughout oxidation of ML added with Q microparticles seemed to show two releasing zones: the first one corresponds to the equilibrium zone, when Q released from microparticles replaces Q that is being degraded; the second zone corresponds to the degradation of Q, when the release rate of the encapsulated Q is slower than its degradation rate. In contrast, E microparticles showed only one zone corresponding to the release of surface E. The end of the induction period was in line with the exhaustion of Q and E and the initiation of formation of advanced oxidation products (polymers). In conclusion, Q microparticles have a potential application to extend the shelf-life of lipid matrixes.

The Impact of Diacylglycerol on Association Colloids Formation and Lipid Oxidation Mizue Ouchi*[1], Eric A. Decker[2], and D. Julian McClements[2], *[1]Kao Corporation, Japan; [2]University of Massachusetts Amherst, USA*

Refined oil contains small amount of water and various kinds of surface active components such as phospholipids. In previous studies, our group reported association colloids such as reverse micelles are formed by these surface active components and affect lipid oxidation. Diacylglycerols (DAG), one of the minor components in refined oils, have different physicochemical properties from triacylglycerols (TAG) due to its structure. There are several studies on the influence of DAG on the oxidation stability. However, little is known about the impact of DAG on association colloids formation, and very few attempts have been made to retard oxidation using minor components for inhibiting association colloids formation. This study focused on how the DAG affect the ability of 1,2-dioleoyl-sn-glycero-3-phosphatidylcholine (DOPC) to form association colloids and lipid oxidation. The critical micelle concentration (CMC) and the mobility of phospholipid in different polar oils were measured by using TCNQ solubilization technique, interfacial tension, and NMR measurement. Higher mobility of phospholipid was confirmed in high DAG concentration oils suggesting the possibility of DAG to inhibit association colloids formation. Oxidative stability was confirmed that DOPC at concentrations above its CMC was prooxidative regardless of the presence of DAG, while high DAG concentration oil could slightly retard oxidative rate when the CMC of the oil was above DOPC concentration in the oil sample. To find out the role of minor components would contribute to develop new strategy to improve oxidative stability.

EAT 3.1a/LOQ 3b: Manufacture and Stabilization of W/O and O/W Emulsions for Optimal Shelf-life

Chairs: Tanu Tokle, Qualitech, USA; Ann-Dorit Moltke Sørensen, Technical University of Denmark, Denmark; and Chandra Ankolekar, Kemin Industries Inc., USA

Stability and Functionality of Colloidosomes as Delivery Systems for Small Molecules Umut Yucel*, *Kansas State University, USA*

Colloidosome particles, similar to Pickering emulsions but with smaller initial adsorption energies can be obtained, by surrounding a core particle by smaller wall-forming particles. We formulated colloidosome particles from base-emulsions prepared with liquid and solid lipids (refined coconut oil composed of lauric and capric acid, and hydrogenated palm stearin), and different emulsifiers (sodium caseinate, pectin, chitosan). The liquid lipid core served to encapsulate small molecules: limonene as a model flavor compound, and a hydrophobic nitroxide radical, PTMIO. Real-time kinetic release of limonene was measured using a mass spectrometer coupled to atmospheric pressure compound ionization (APcI-MS), and compared to the phase behavior and reactivity of PTMIO as analyzed by an electron paramagnetic resonance (EPR) spectrometer. The base-emulsions prepared at two particle sizes 160 nm to 600 nm. The net surface charge of the caseinate emulsions was –40 mV at pH 6.5, and +25 mV at pH 3.5, pectin emulsions –30 mV at pH 3.4, and chitosan emulsions +35 mV at pH 3.5. The particle aggregates formed by controlled mixing of emulsions with opposite surface charge, and observed as an increase in the apparent particle size (> 1000 nm). The formation of a solid wall limited the release of limonene, which regenerated by removal of the wall with pH or thermal changes. The behavior of PTMIO was similar to limonene as monitored by deconvolution of the complex EPR spectra to individual signals coming from aqueous and lipid phases. Such systems can be used to encapsulate labile small molecules, and their targeted delivery.

Impact of Phospholipids and Tocopherols on the Oxidative Stability of Soybean Oil-in-Water Emulsions Gautam Samdani*, D. Julian McClements, and Eric A. Decker, *University of Massachusetts Amherst, USA*

Phospholipids can regenerate oxidized tocopherols and help delay lipid oxidation. Extent of synergism between tocopherol, phosphatidyl-ethanolamine(PE) and phosphatidylserine(PS) is affected by various factors like the location of antioxidants. Emulsifier type and tocopherol homologue can alter the location of antioxidants and affect the interactions between tocopherol and phospholipids. Three µmol tocopherol/kg emulsion and 15.0µmol/kg emulsion of PE or PS were dissolved in oil and emulsions were prepared. Tween 20 or bovine serum albumin(BSA) was used as emulsifier and the continuous phase contained 10mM imidazole/acetate buffer at pH 7. Lipid hydroperoxides and hexanal were measured as lipid oxidation products and the lag phase was determined. Further investigation was carried out to find the partitioning of phospholipids in the aqueous phase to understand the mechanism. With Tween 20 as the emulsifier, α and δ-tocopherol had a hexanal lag phase of

2 and 4 days respectively. PE and PS both extended the lag phase to 7 days in presence of δ-tocopherol. Whereas, PS extended the lag phase to 5 days and PE could not exhibit any synergism with α-tocopherol. With BSA as the emulsifier, α and δ-tocopherol had a lag phase of 4 and 7 days respectively. PE and PS extended the lag phase to 8 days and 11 days respectively in presence of δ-tocopherol and to 9 and 8 days respectively in presence of α-tocopherol. Phospholipids could potentially be used with tocopherols to improve the oxidative stability of emulsions. PE was more effective with BSA whereas PS was equally effective with both emulsifiers.

Effect of Droplet Size and Interfacial Crystallization on the Rheology of Fat Crystal-stabilized Water-in-Oil Emulsions

Dérick Rousseau* and Ruby R. Rafanan,
Ryerson University, Canada

Water droplets as rheology modifiers in fat crystal-stabilized emulsions is a novel research area. This study investigated how fat crystal-stabilized emulsion rheology is impacted by aqueous droplet interactions with continuous phase fat crystals. 20% water-in-oil emulsions were prepared with the continuous phase consisting of canola oil, hydrogenated soy oil (HSO) and one of 3 emulsifiers: glycerol monooleate (GMO) and glycerol monostearate (GMS) to promote interfacial crystallization, and polyglycerol polyricinoleate (PGPR) to limit it. Small (Sm) and large (Lg) droplet size distributions (DSD) were prepared for each surfactant. LgDSD and SmDSD GMS emulsions displayed the highest LVR G' values followed by GMO and PGPR. Reinforcement ($R = G'_{emulsion}/G'_{network}$) values increased for each surfactant over time. On day 0, R values for SmDSD were higher than LgDSD for PGPR and GMO stabilized emulsions. The reverse was observed for GMS-stabilized emulsions. By day 28, both SmDSD and LgDSD GMS emulsions reached similar R maxima. Similar trends, but lower R values were observed for GMO emulsions. PGPR emulsions displayed the least reinforcement and least effect of DSD. Power-law fitting of viscosity showed that DSD did not affect shear thinning behaviour within surfactants. Consistency followed similar trends to G' and reinforcement. This experiment showed that the interface and droplet size impact overall consistency and reinforcement in droplet filled emulsions, most significantly in freshly-made emulsions. By considering the droplet interface as a tunable, functional component within a network, it is possible to create novel fat-stabilized emulsions with desired consistencies without changing characteristics such as solid fat content.

Label Friendly EDTA Alternative for Oxidative Stability Improvement in Food Emulsions

Lan Ban*, Yvonne Gildemaster, and Joan Randall,
Kemin Food Technologies, USA

Chelating agents like ethylenediaminetetra-acetic acid (EDTA) sequester metal ions and are widely used as antioxidant in food emulsions. EDTA is very cost effective for the quality of processed foods. However, it has posed a negative image, especially in the consumer food sector, that arises from its synthetic origin, non-biodegradable nature, and being a possible environmental hazard. Major players in the food industry have placed it in the list of ingredients that manufacturers are removing in the next few years. On the other hand, there is no effective

replacement yet that could be validated to match the performance of EDTA, especially in acidic processed foods. The objective of this study was to find natural ingredients that match the performance to EDTA, from the same chelating function or from different modes of actions. Various natural plant extracts were screened and three candidates (spearmint extract, green tea extract and rosemary extract) were evaluated further as combinations aided by Design of Experiment. The best combination and dosage were identified and validated in mayonnaise and ranch dressing systems. The results have shown that first, there was a positive correlation between the dosage of this blend and its performance. Second, the major driven force of antioxidant potential was from spearmint extract. Third, at the treatment level that was slightly below its flavor threshold, this blend was very close in performance to EDTA in mayonnaise. The continuation of this work will hopefully to provide the consumer food industry with label friendly options to replace EDTA.

LOQ 4a: Lipid Oxidation in Complex Food Products and Interactions with Ingredients

Chairs: Linhong Yao, Mondelēz International Inc., USA, USA; and Lan Ban, Kemin Food Technologies, USA; and Will Schroeder, Kemin Food Technologies, USA

Lipid Oxidation in Fish Feed. Ann-Dorit Moltke Sørensen, Anita Ljubic, and Charlotte Jacobsen*, *Technical University of Denmark, Denmark*

Lipid oxidation in fish feed is influenced by many different factors including choice of ingredients and antioxidant addition. In this study we evaluated the effect of adding blood meal to fish feed as well as different antioxidants. The extent of oxidation was evaluated by Oxypress. Furthermore, a storage study at elevated temperature was carried out and lipid oxidation was assessed by PV and TBARS.

The Combination of Green Tea and Rosemary—Impact of System, Concentration and Ratio on Antioxidant Performance Xin Tian, Nora Yang, and Poulson Joseph, *Kalsec Inc., USA*

Green tea extract and rosemary extract are two popular ingredients among the choice of natural antioxidants, because of their strong efficacy and clean label image. They have been studied individually by a number of researchers but very few studies have looked at the interaction of the two antioxidants. Combinations of rosemary and green tea extracts were tested in different applications such as bulk oil, meat and dry foods. Green tea extract was formulated with low HLB emulsifiers in order to improve its oil solubility and to facilitate its application in oils and oil-containing foods. Both synergistic and antagonistic effects were observed. The food systems, concentrations and sometimes ratio of the two components all play a role in impacting the efficacy of the blends. This research is useful in guiding the application of these natural antioxidants to achieve optimum performance in various applications.

Evaluation of Antioxidants and Antimicrobials from Plant Extracts in Pet Food Charlotte Deyrieu[1], Erwann Durand[1], Nathalie Barouh[1], Jerôme Lecomte[2], Françoise Michel-Salaun[3], Bruno Baréa[1], Gilles Kergourlay[3], and Pierre Villeneuve[1], *[1]CIRAD, France; [2]CIRAD, Greece; [3]Videka Diana Pet Food, France*

Lipid oxidation and Microbial development are a major concern in human's food. However, it is not the only sector where they are an issue, since the pet food market is also deeply affected. Pet food products are composed of oils and fats which contribute to their flavor, nutritional value, and texture. During the pet food manufacturing process, lipids are exposed to conditions promoting their oxidation which leads to rancidity, creates off-odors and lower food nutritional value. As in human food, the lipid oxidation may be delayed through the incorporation of antioxidants, and consumers frequently ask for natural solutions as an alternative to synthetic preservatives. Similarly, new efficient antimicrobial molecules are needed. As a consequence, pet food manufacturers are now tasked with improving the efficacy of natural antioxidants and antimicrobials. In this context, the present study went to investigate strategies to formulate pet food with highly effective antioxidants/ antimicrobials from natural sources. Thus, the efficacy of various plant extracts has been tested in different model assays.

Non-targeted Screening for Oxidized Lipids in Foods Charlotte Deyrieu[1], Erwann Durand[1], Nathalie Barouh[1], Jerôme Lecomte[2], Françoise Michel-Salaun[3], Bruno Baréa[1], Gilles Kergourlay[3], and Pierre Villeneuve[1], *[1]CIRAD, France; [2]CIRAD, Greece; [3]Videka Diana Pet Food, France*

Consumption of oxidized fats is known to have detrimental as well as beneficial effects. Studies on structural elucidation of individual oxidized lipids formed during food processing are missing. Thus, a thorough identification of oxidized lipids present in foods is required. We aimed at identifying oxidized triacylglycerols in thermally treated canola oil, pork, salmon, milk, butter and margarine by means of high-resolution MS applying non-targeted screening. Changes in the abundances of oxidized triacylglycerols in differently heat-processed food samples were determined by LC-MS/MS. Besides many hydroperoxides, several epoxidized triacylglycerols could be identified, such as 18:0-18:0-18:0 monoepoxide, 18:0-18:1-18:0 monoepoxide, 18:0-18:1-18:1 monoepoxide, 18:1-18:1-18:1 monoepoxide and 18:1-18:2-18:2 monoepoxide. Among all tested food lipids, canola oil showed to have the highest abundance of oxidized lipids even under non-thermally treated conditions at 25°C. While most epoxidized triacylglycerols decreased by approximately 80% after thermal treatment at 180°C for 30 min, 18:0-18:1-18:1 monoepoxide did not change significantly, indicating a probable structure-specific formation and decomposition rate of oxidized lipids. Interestingly, epoxidized triacylglycerols almost completely vanished after thermal treatment at 80°C for 30min whereas at 180°C these oxidized lipids were more abundant. Taken together, oxidized triacylglycerols could be identified in food lipids under household-representative food processing. LC-MS/MS is a valuable approach to characterize the quality of food lipids and identify their oxidized triacylglycerol profile, which is of relevance to evaluate the biological effects of different oxidized lipids.

Polyphenol Shifts in Lipid Oxidation Pathways and Interactions with Proteins Alter Apparent Antioxidant Effectiveness Karen M. Schaich*[1] and Xiaosong Chen[2], *[1]Dept. of Food Science, Rutgers University, USA; [2]China Agricultural University, China*

Natural phenolic compounds are very attractive as alternatives to BHA and BHT in limiting lipid oxidation but have often been disappointing in their effectiveness in foods. At the same time, reports of pro-oxidant actions of phenols have increased. Research in model systems provides new insights into the complexity of phenol interactions. Studies of alternate competing pathways of lipid oxidation show that phenols can reroute epoxide formation (by peroxyl radical addition to double bonds) to hydroperoxide formation via H abstraction from phenols. When hydroperoxides are the only product analyzed, lipid oxidation then appears to be paradoxically increased. Alkoxyl radicals are similarly rerouted away from rearrangement (epoxides) and scissions (aldehydes and alkanes) to H abstraction generating hydroxylipids, an antioxidant action with most analyses. Phenolic compounds react with proteins as well as lipids. Gallic acid, pyrogallol, hydroquinone, resorcinol, catechol, caffeic acid, para-coumaric acid, and ferulic acid induced denaturation of highly purified alpha-lactalbumin in phosphate buffer, with major changes in protein configuration plus dramatic

losses of tryptophan, free amines, sulfhydryls, and disulfides. This action diverts radical quenching by phenols away from lipids and blocks H donations from protein sites (lipid pro-oxidant) but also blocks lipid co-oxidation of proteins (antioxidant to total food system). These actions together greatly complicate effects of phenolic compounds in foods and argue for broader analyses, beyond just lipid hydroperoxides and hexanal, to accurately track and fully elucidate how antioxidants alter food chemistry.

EAT 4.1/LOQ 4b: Food Structuring to Reduce Lipid Oxidation

Chairs: Hong-Sik Hwang, USDA, ARS, NCAUR, USA; and Alex Kripps, Caldic USA, USA; and Yaqi Lan, South China Agricultural University, China

Formation of Free-flowing Fish Oil-loaded Hollow Solid Lipid Micro- and Nanospheres Using Carbon Dioxide Junsi Yang and Ozan N. Ciftci*, *University of Nebraska-Lincoln, USA*

Effectively incorporating fish oil into foods and beverages is a major challenge due to their low water solubility and easy degradation during processing and storage. Therefore, the objective of this study was to develop novel free-flowing fish oil-loaded hollow solid lipid micro- and nanospheres (HSLS) that can be added into foods and beverages.

Fish oil was loaded into HSLS in a single step process based on atomization of the CO_2-expanded fully hydrogenated soybean oil. Fish oil-loaded HSLS ($d_{50\%}$= 5.6 µm) were obtained using 50 µm nozzle diameter and 200 bar expansion pressure, with loading efficiencies up to 97%. All particles were spherical and in the dry free-flowing form. Surface with wrinkles was observed when the initial fish oil concentration was increased to 50%. Shell thickness of the spheres increased with decreasing pressure. Onset melting temperature of the fish oil-loaded HSLS decreased from 66ºC to 62ºC with increasing fish oil content, while major polymorphic form transformed from α to β. The loaded fish oil showed increased oxidative stability compared to crude fish oil ($p<0.05$). Nanospheres were successfully separated from microspheres by filtration, and formed clear liquid when added into water.

This innovative method forms free-flowing powder products that are easy-to-use solid fish oil formulation, which makes the handling and storage feasible and convenient. Hollow structure provides high loading capacity, solid shell protects sensitive bioactive, and nanosize allows transparent beverage preparation using water-insoluble bioactives. Moreover, the process is simple and green, no toxic solvent is used.

Natural Wax Oleogels-A Method to Prevent Oxidation of Fish Oil Hong-Sik Hwang[1], Matthew Fhaner[2], Jill Moser[1], and Sean Liu[3], *[1]USDA, ARS, NCAUR, USA; [2]University of Michagan-Flint, USA; [3]USDA, ARS, USA*

Oleogels (or organogels) are formed by immobilization of oil by an oleogelator. Therefore, it was hypothesized that immobilization of oil could also prevent the oxidation of oil. This study was focused on preventing oxidation of fish oil, an omega-3 oil, due to its beneficial health effects such as reducing the incidence of heart attacks, reducing inflammation and the brain development in fetuses. This study also aimed to provide useful information on oxidation of oleogels, which are promising alternatives to trans/saturated fats. Fish oil oleogels were prepared with four different natural waxes, rice bran wax, sunflower wax, candelilla wax, and beeswax. Oil oxidation was monitored with peroxide value, conjugated diene value, eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA) at 35°C and 50°C. 3% wax-fish oil oleogels showed slower oxidation than the bulk fish oil at 35°C. The melting point is an important factor when choosing wax for this method at higher temperatures since beeswax

was not as effective as other waxes at 50°C due to its lower melting point. A new analytical method, color penetration measurement method, was developed in this study, which can be used to predict the oxidation rate of oleogel. Cooling oleogel at a faster rate could significantly reduce the oxidation rate of the oleogel. Prooxidant activity of wax was observed and therefore, a larger amount of wax is not recommended to increase the protective effect.

Self-assembled Colloidal Complexes of Polyphenol–gelatin and their Stabilizing Effects on Emulsions Chaoying Qiu, Yu Huang[1], Zhen Zhang[2], Ying Li[3], and Yong Wang[1], *[1]Jinan University, China; [2]South China University of Technology, China; [3]Guangdong Saskatchewan Oilseed Joint Laboratory, Dept. of Food Science and Engineering, Jinan University, China*

This research studies the in-depth characteristics including the binding interactions and morphological structure of tannic acid (TA)/grape seed proanthocyanidins (GSP) and gelatin (GLT) colloidal complexes, and evaluated the stability and lipid oxidation of emulsions formed by the colloidal complexes. Polyphenol and GLT (1.2 wt%) self-assembled complexes were fabricated by varying the mass ratio (1 : 16, 1 : 8 and 1 : 4) and pH in the range of 3–7. TA and GSP can form stable colloidal complexes with GLT at the nanoscale at pH 6, as shown by the particle size results, and the complexes exhibited a spherical morphology as seen by transmission electron microscopy. Hydrogen bonding was the main binding force for the interaction between polyphenols and GLT. The antioxidant activity of GLT was greatly improved after complexing with polyphenols. The oil/water emulsion formed by the complexes had a smaller droplet size and higher lipid oxidation stability during storage. This was largely due to the physical barrier formed by polyphenol–GLT colloidal complexes at the oil–water interface, which can prevent the pro-oxidant from penetrating into oil. These results clarified the structural, morphological and antioxidant properties of polyphenol–gelatin non-covalent complexes, which is of great value for their application in food solutions as well as in emulsion systems.

Ability of SDS Micelles to Increase the Antioxidant Activity of α-tocopherol Raffaella Inchingolo[1], Sezer S. Kiralan[1], Sibel Uluata[1], MariaTeresa Rodriguez Estrada[2], D. Julian McClements[3], and Eric A. Decker[3], *[1]University of Massachusetts, USA; [2]University of Bologna, Italy; [3]University of Massachusetts Amherst, USA*

The physical location of antioxidants in oil-in-water (O/W) emulsions can affect their ability to inhibit lipid oxidation. In this study, the effect of sodium dodecyl sulfate (SDS) below and above its critical micelle concentration (CMC) on the partitioning behavior of α-tocopherol in stripped soybean O/W emulsion was investigated. Aqueous phase partitioning of lipophilic α-tocopherol (70%) was observed at levels above SDS CMC (5–7 mM). Subsequently, the impact of antioxidant location and SDS concentration on antioxidant activity was determined by monitoring the formation of lipid hydroperoxides and headspace hexanal in emulsions. Results showed that lag phase extension of lipid oxidation increased when tocopherol was solubilized in SDS micelles. The mechanism of increased tocopherol activity at high SDS concentrations was further investigated in O/W emulsions made from medium chain triaclyglycerols (a non-oxidizable lipid). Tocopherol location and concentration were

monitored over 32 hours in emulsions with and without the presence of the metal chelator EDTA. Results suggest that SDS above its CMC decreased aqueous phase tocopherol degradation and that tocopherol loss was largely due to aqueous metal initiated free radicals. Overall, these results show that micelle solubilization of tocopherol into the aqueous phase by an emulsifier (SDS) greatly enhanced the ability of tocopherol to inhibit lipid oxidation. Data presented herein suggests that this technology could be used to increase the activity of tocopherols that are naturally found in foods.

Impact of Reduced Oxygen Environment and Natural Antioxidants on the Oxidative Stability of Oil-in-Water Emulsions Eric A. Decker[1] and David R. Johnson*[2] [1]*University of Massachusetts Amherst, USA;* [2]*Kalsec Inc., USA*

Consumer concerns over synthetic food antioxidants have led researchers to seek alternative natural, or 'clean' label, solutions to prevent lipid oxidation in emulsified systems. Developing natural antioxidant strategies for emulsified systems is particularly difficult due to increased surface area, presence of transition metals, and decreased efficacy compared to synthetic antioxidants. As a result, there remains a need to develop new strategies and optimize current antioxidant strategies in oil-in-water (O/W) emulsion applications. In previous work, it was shown that 1% fish O/W emulsions that were packaged with total oxygen reduction concentrations of ≥93% exhibited a three-fold increase in oxidative stability compared to saturated oxygen conditions. Unfortunately, reaching total package oxygen reduction concentrations of ≥93% may not be cost effective or even a feasible strategy for emulsified foods. Total package oxygen reduction concentrations of 60-80% may be more practical. In the present work, the impact of how naturally derived polar and nonpolar antioxidants function under saturated and 60-80% reduced oxygen atmospheres in 1% stripped fish O/W emulsions was determined. Lipid oxidation, as measured by lipid hydroperoxides and TBARS, was inhibited by lipophilic antioxidants in O/W emulsions whereas aqueous phase antioxidants promoted lipid oxidation. Notably, the combination of 60–80% O2 reduction did not appear to enhance functionality of the natural antioxidants. Further studies of O/W emulsions using natural extracts in more complex emulsified matrices (mayonnaise) demonstrated the effectiveness of natural antioxidants compared to the synthetic additive EDTA. Results presented provide a reference for efficacy of natural antioxidants in model and complex emulsified matrices.

LOQ 5a: Oxidation By-products in Food and Feed: Impact on Nutritional Value and Metabolic Processes

Chairs: S.P.J. Namal Senanayake, Camlin Fine Sciences, USA; and Constantin Bertoli, Nestle Product Technology Center, Switzerland

Nutritional Impacts of Oxidation Byproducts in Food: The Pet Food Dilemma Megan E. Morts* and Greg Aldrich,*Kansas State University, United States*

Modern pet foods have evolved from kibbles and cans to raw, frozen, and freeze-dried meat-based options. There has also been pressure to shift away from synthetic preservatives simultaneous to a demand for shelf-life nearing two years. Stability of these new food forms has not been effectively evaluated. In comparable human meat-based products it has been shown that repeated freezing and thawing can increase oxidation measured as TBARS by as much as 500% from baseline. Even for meat stored at 4°C a drastic increase can occur in less than 10 days. Packaging and air exclusion may help, but modified atmosphere technology may have less impact than vacuum sealed meats. Much of this oxidation described for meats could occur in pet foods and lead to physiological effects that impact the acceptability, nutrition, and safety of food for companion animals. This review will focus on the impact that extended time in storage has on the oxidation of food intended for pets. How it affects essential vitamins and fatty acids, the impact on sensory attributes of the food for both pet and owner, and the potential for harmful substances that could be deleterious to animal health and wellbeing. Finally, a discussion regarding the mechanism of action for these effects and suggestions will be offered for alternative markers of quality that should be considered for determining the quality and consistency of the products produced and offered to the market for the long-term nourishment of dogs and cats.

Dietary Intake of Mildly Oxidized Fat Increases Colitis and Colitis-associated Colon Tumorigenesis through Activation of Toll-like Receptor 4 (TLR4) Signaling Weicang Wang, Yuxin Wang, Eric A. Decker, and Guodong Zhang*, *University of Massachusetts Amherst, USA*

Background: In the last century, there has been a dramatic increase in the incidence and prevalence of inflammatory bowel disease (IBD) in US and other countries. Emerging evidence supports that environmental and dietary factors are primarily responsible for the growing incidence of IBD. It is important to identify these risk factors, in order to develop targeted strategies for prevention. In this study, we examined whether oxidized dietary fats, which are commonly found in a typical Western diet, are capable of exaggerating colonic inflammation and colon tumorigenesis. Methods: We purified commercial vegetable oil by silicic acid-activated charcoal chromatography to prepare un-oxidized oil, which was then oxidized to prepare the oxidized oil. We then evaluated the effects of un-oxidized and oxidized vegetable oils on dextran sodium sulfate (DSS)- and IL-10 knockout-induced colitis, and azoxymethane (AOM)/DSS-induced colon tumorigenesis in mice, and studied the roles of Toll-like receptor 4 (TLR4) signaling

involved. Results: Treatment with oxidized vegetable oil, even at low oxidative status (within the recommended industrial limit of the oxidative status of vegetable oil), increased DSS- and IL-10 knockout-induced colitis and AOM/DSS-induced colon tumorigenesis in mice. Oxidized vegetable oil increased activation of TLR4 signaling in the systemic circulation, by disrupting intestinal barrier function and thus enhancing circulating levels of lipopolysaccharide (LPS) and bacteria, and the pro-colitis effect of oxidized vegetable oil was abolished in TLR4 knockout mice. Conclusion: Oxidized vegetable oil, even at low oxidative status, could be a risk factor of IBD and associated colon cancer.

Implications of Feeding Peroxidized Lipids in Swine Brian Kerr*, *USDA-ARS, USA*

Optimal nutrient utilization by farm animals is essential for supporting growth and development and is vital in maintaining economical animal production. While profiles, digestibilities, and balances of energy and nutrients of feedstuffs are critical in the nutrient utilization matrix, so is the ability of the animal to balance mechanisms generating oxidative stress with antioxidant defenses within the body. Pro-oxidants can be of environmental, dietary, or metabolic origin, where oxidative stress occurs when free radical production overwhelms the antioxidant defense system. In livestock, lipids are a concentrated source of energy, but the composition of a lipid and how it has been processed may affect its value in feed formulations. Recent research in this laboratory has focused on the process of lipid peroxidation, largely soybean oil, and key measures within the lipid which may be predictive of their negative on animal productivity. Along with the overall impact of peroxidized lipids on growth performance, an accurate determination of oxidative balance in the whole animal was assessed using multiple measures of lipid, protein, or DNA damage. This presentation will discuss recent research using peroxidized lipids in nursery, grower, and finisher pigs as an inducer of oxidative stress and key measures of lipid peroxidation and oxidative stress which should be considered in animal production.

Food-induced Formation of Health-damaging Compounds during Repeated Deep-fat Frying Cycles Ru Shen, William G. Helferich, and Nicki J. Engeseth, *University of Illinois at Urbana-Champaign, USA*

Repeat-utilization of frying oil, TAFO (thermally abused frying oil), results in undesirable compound formation; this is impacted by the fried food matrix. The overall goal of this research was to determine the specific food-induced formation of undesirable components in TAFO. The central hypothesis was that undesirable compounds formed during repeat frying would differ based upon the foods fried. Frying experiments were conducted with 60 deep-fat frying cycles of chicken and fish in soybean oil with control oil heated separately without food. Oil and foods were periodically analyzed. For undesirable compounds, including EFA (epoxy fatty acids) and aldehydes in TAFO were characterized using GC and HPLC. Repeated exposure to high-temperature frying led to significant deterioration of oil with increased total polar compounds (TPC: 4.35-11.93%). Control heated oils maintained quality (TPC: 2.86-3.10%). Chicken frying resulted in greater increase in TAFO free fatty acids. Fish resulted in a more dramatic increase in TAFO peroxide and

p-Anisidine values than chicken. This result is consistent with oxidation product formation. TAFO accumulation of EFA was in the order of fish (145.01–451.36 µg/g oil)> chicken (152.34–543.32 µg/g oil) > control (104.89–163.80 µg/g oil). By contrast, EFA accumulation in fried food was greater in chicken (82.50–143.35 µg/g food) than fish (57.34–137.71 µg/g food). To conclude, frying oil deterioration was highly dependent upon the type of food fried. Fish frying contributed greater to oxidative instability whereas chicken contributed more to hydrolytic instability. Considerable accumulation of health-damaging undesirable compounds both in foods and oils during repeated deep-fat frying deserves more attention.

LOQ 5b: Lipid Oxidation and Quality General Session

Chairs Jill Moser USDA, ARS, NCAUR USA

Synergism and Antagonism of Phenolic, Amine and Sulfur-containing Antioxidants in Lipid Oxidation Olga T. Kasaikina and Karina M. Zinatullina, *Semenov N.N. Institute of Chemical Physics, Russia*

Combinations of antioxidants (AO) may cause a great variety of interactions among them resulted in additivity, synergism, when the whole effect exceeds the sum, or antagonism, when the whole AO effect is less than sum of retardation effects. Synergistic mixtures of AO allow the use of lower doses of the combination AO, a situation that may reduce adverse reactions and the economic costs. Mixtures of the phenolic AO and sulfur-containing compounds are well-known synergistic combinations for polymer and industrial oils stabilization. Currently, there is a steady trend in the use of natural products in innovative technologies for the creation of healthy and healing foods, cosmetics, medicines containing essential unsaturated lipids and natural antioxidants because of consumer demand for natural ingredients. This short topic presents the current our studies of pro- and antioxidant properties of individual natural thiols (cysteine, homocysteine, mercaptoethanol and especially, glutathione) and their interaction with different phenolic and amine AO, the thiol-en reactions between glutathione and phenols containing double bonds in their structure (resveratrol, hydroxy-derivatives of cinnamic acid). The mutual influence of the AO and lipid metabolites and the conditions of occurrence of synergism and antagonism in the prevention of oxidation of a complex system {Mixture of AO-Lipids} is discussed as well.

Physical and Oxidative Stability of O/W Emulsions Stabilized by Gum Arabic Glycated Pea Proteins Bingcan Chen and Fengchao Zha*, *North Dakota State University, USA*

In recent years, there is a strong interest in replacing animal-based protein emulsifier by plant proteins due to cheaper price and more sustainable source with a lower carbon footprint. However, poor functionality such as acidic solubility and thermal stability limits the application of pea protein as emulsifier in food industry. The aim of the present study was to modify pea proteins, including pea protein concentrate, pea protein isolate and hydrolyzed pea protein through glycation reaction with gum arabic. The influence of glycated pea protein on the physical properties and oxidative stability of soybean oil-in water emulsions was fully investigated. The results suggested that reaction time and pea protein type will impact the color intensity of glycated products, the emulsion physical stabilities against environmental stress including pH, thermal processing, and salt concentration, and the oxidative stability of the emulsions. This study indicates that glycation reaction is an efficient meaning to enhance the functionality of pea proteins to stabilize food emulsions.

Oxidative Stability of Flaxseed Oil: Effect of Polar, non-Polar and Surface Active Antioxidants Athira Mohanan, Michael Nickerson, and Supratim Ghosh, *University of Saskatchewan, Canada*

High susceptibility towards oxidative deterioration is a major issue limiting the

utilization of flaxseed oil (FSO). Present study explored the use of several natural antioxidants and a synthetic antioxidant (tert-butylhydroquinone (TBHQ)) on the oxidative stability of flaxseed oil. After an initial screening of DPPH radical scavenging and metal chelating abilities of several polar (tannic acid, caffeic acid and L-ascorbic acid), non-polar (alpha tocopherol, eugenol, and beta carotene), and amphiphilic (ascorbyl palmitate and quercetin) antioxidants, the best from each category (tannic acid, alpha tocopherol and ascorbyl palmitate) was selected. The effects of different concentrations of the selected antioxidants on FSO oxidation was examined by measuring peroxide and p-anisidine values during long-term storage (30 d) at 25, 40 and 60°C. Accelerated oxidation tests were also performed using a rancimat at 100°C. All natural antioxidants were less effective than TBHQ in preventing oxidation of FSO. At 400 ppm concentration, the time to induce accelerated oxidation of FSO increased from 2.4 h to 29 h with TBHQ, 18 h with ascorbyl palmitate and 5 h with tannic acid. Irrespective of the polarity, all natural antioxidants, except alpha tocopherol delayed primary and secondary oxidation of FSO during storage at all temperatures, but the effect was less than TBHQ. The alpha tocopherol displayed pro-oxidant effect at all concentrations. The study revealed that, along with high antioxidant capacities, ability of the antioxidant to replace minor components from the moisture-oil interface and minimal antioxidant-metal interaction were also crucial for the protection of FSO.

Antioxidant and Antibacterial Activity of Different Extracts from Herbs Obtained by Maceration or Supercritical Technology

Ignacio Vieitez*, Lucía Maceiras, Iván Jachmanián, and Silvana Alborés, *UdelaR, Uruguay*

Viability of obtaining extracts that are rich in natural antioxidants is known from many common herbs and spices, which can be used in the food industry. Such extracts can be efficient, providing protection against harmful free radicals and, additionally, they provide an alternative to synthetic antioxidants, answering the consumers' increasing demand for additive-free or natural products. Supercritical fluid extraction with carbon dioxide has been demonstrated to be an attractive method to apply to the different processes involved in the food industry. It presents several advantages when compared with conventional organic solvents. Supercritical CO2 extracts from Rosmarinus officinalis, Peumus boldus, Aloysia citrodora, Maytenus ilicifolia, Ilex paraguariensis and Eugenia uniflora were obtained at different extraction conditions and their antioxidant effect was determined. Results were compared with that obtained with extracts from traditional solvent maceration methods and with that shown by different common synthetic antioxidants. Additionally, antibacterial activity of extracts from the different herbs obtained was determined against different microorganisms. Extraction efficiency increases with increasing polarity of the solvents used; however, not all of the compounds extracted are active, evidencing this in the antioxidant capacity of the extracts.

Some of the extracts were as effective or more effective than some of the synthetic antioxidants commonly used like BHT and BHA. Therefore, supercritical extracts from these herbs were efficient in protecting sunflower oil against oxidation; thus, they could represent a valuable natural alternative to synthetic antioxidants. Additionally, herbal extracts proved to be a source of compounds with antibacterial activity, with promising applications in the control of microbial deterioration of food.

LOQ-P: Lipid Oxidation and Quality Poster Session

Chair: Uwe Nienaber, DSM Nutritional Products, USA

1. **A Comparison of Commercial Enzymes Used Individually or in Combination for Aqueous Enzymatic Extraction of Oil from Njangsa Seed.** Mary Besong[1], Anh Nguyen[2], Samuel A. Besong[2], and Alberta N.A. Aryee*[2], *[1]The Henry P. Becton School of Nursing & Allied Health, Fairleigh Dickinson University, USA; [2]College of Ag. & Related Sciences, Dept. of Human Ecology Delaware State University, USA*

Njangsa (*Ricinodendron heudelotti*) seed is a staple ingredient used in many cuisine throughout Africa. Njangsa seed oil (NSO) has been shown to be rich in polyunsaturated fatty acids. Solvent extraction, commonly employing hexane is one of the main conventional method used for oil extraction from oilseeds. However, exposure to solvents poses health risk and has negative impact on the environment. To preclude these repercussions, enzyme-catalyzed oil extraction emerges as one of the most environmentally friendly alternative method to solvent oil extraction. In this study, four enzymes; hemicellulase, amylase, protease and pectinase were used in singly or in combination (combinations of two enzymes, three enzymes, and all four enzymes together) to extract NSO, and the recovery and quality indices of the oil were determined. Up to 41.78% of oil was recovered from the seeds. The quality indices of the oil such as free fatty acid (FFA) content, peroxide value (PV), and thiobarbituric acid (TBA) value ranged from 1.61 to 6.77%, 7.89 to 59.06¬ mEq of peroxides/kg of oil, and 0.03 to 0.2 mg of malonaldehyde/kg of oil, respectively. Free fatty acid (FFA) content and PV were significantly ($P<0.05$) affected by the type of enzymes used, whilst, TBA values was not significantly ($P>0.05$) affected by the type of enzyme used. The results obtained from this present study indicate that oil extracted using these enzymes were qualitatively and quantitatively different and combine use of enzymes resulted in improved oil recovery.

2. **Impact of High Pressure and Temperature Processing on Antioxidant Activity of Canola Meal Extracts.** Ruchira Nandasiri, Erika Zago, and Usha Thiyam, *University of Manitoba, Canada*

Canola (*Brassica napus*) meal is a by-product of the bio-refinery and a rich source of polyphenols. Canolol is a phenolic derivative from sinapine (main canola phenolic). The antioxidant properties of canolol were established and it was found that scavenging properties are comparatively higher than other phenolic compounds together with carotenes and tocopherols. Although there are numerous studies associating the impact of high temperature processes to the canola phenolic profile, up to date a limited number of studies are available to identify the structure elucidation of antioxidant compounds related to accelerated solvent extraction (ASE). It is assumed that the improvement of the antioxidant properties of canola extracts could be related to the production of canolol and other novel compounds as canolol dimers and trimers. The current study was conducted to identify the structure-function relationship of the phenolic compounds in canola meal extracts during ASE. Canola meal was treated with three different temperatures (140°C, 160°C, 180°C) to identify the structural alterations associated with

antioxidant activity. Antioxidant properties were evaluated through FRAP, DPPH and metal ion chelation activity. In addition, total phenolic contents (TPC) and total flavonoid contents (TFC) were investigated to identify the structure elucidation properties. The quantification of individual phenolic compounds was carried out through a novel HPLC method with enhanced selectivity and separation. Results indicated that increases on temperature could improve antioxidant activity, TPC and TFC. Thus, further researches are required to recognize the novel individual phenolic compounds and their potential antioxidant properties in relation to the use of ASE.

3. **Chemometric Comparison of Aldehyde Formation in Olive Oil and Camellia Oil at Frying Temperature.** Ling Peng, Jieyao Yuan*, and Chi Chen, *University of Minnesota, USA*

Under thermal stress, cooking oils can form diverse lipid oxidation products, including reactive aldehydes. Olive oil and camellia oil, as two regional cooking oils in Europe and East Asia, respectively, share similar lipid profiles, especially in the enrichment of oleic acid. However, the kinetics of aldehyde formation in these two oils at frying temperature have not been examined previously. In this study, virgin camellia oil and virgin olive oil were heated from 22˚C to 185˚C, and then kept at 185˚C for 6 h. The aldehydes and free fatty acids in heated oils were derivatized by 2-hydrazinoquinoline and then determined by liquid chromatography-mass spectrometry (LC-MS) analysis. The chemical profiles of heated oils were characterized by principal component analysis (PCA) and hierarchical cluster analysis (HCA). Among identified aldehydes, the levels of pentanal, nonanal and 2,4-decadienal peaked at early time points and decreased afterwards while 2-nonenal, 2-decenal, and 2-undecenal increased continuously at 185˚C. The distribution pattern of olive and camellia samples in the PCA model indicated that major compositional changes occurred at 165 ˚C in olive oil, but did not occur until 185˚C in camellia oil. At 185˚C, multiple aldehydes, such as 2,4-heptadienal, were produced at a faster rate in olive oil than that in camellia oil. Moreover, olive oil contains higher levels of free α-linolenic acid and palmitoleic acid than camellia oil. Therefore, the differences in low-abundance fatty acids might contribute to the differences in thermostability between the examined olive oil and camellia oil.

4. **Chemometric Profiling of Aldehyde Distribution in Frying Oil and French Fries.** Lei Wang, Yuyin Zhou*, Yukari Yamashita, and Chi Chen, *University of Minnesota, USA*

Under frying condition, unsaturated fatty acids undergo peroxidation and degradation to form reactive and cytotoxic aldehydes. Because fried foods contain significant amount of frying oil, the transfer of reactive aldehydes from oil to food is expected. However, the profile of aldehydes in fried food (AFF) as well as its correlation with the profile of aldehydes in frying oil (AFO) remain to be determined. In this study, French fries were prepared at the time points of 5 min, 30 min, 1 h, 2 h, 4 h, and 6 h after heating soybean oil to the frying temperature (185 ± 5°C) in a deep fryer. The AFO in heated soybean oil and the AFF in French fries oil extracts were quantified and compared by the liquid chromatography-mass spectrometry (LC-MS)-based chemometric analysis. The results showed that majority of the AFO in heated soybean oil

and the AFF in French fries increased time-dependently, but in different patterns. The concentrations of AFF in French fries were much lower than that of AFO in heated soybean oil. More importantly, a comparison of the AFF/AFO ratios of individual aldehydesindicated that the efficiency of transferring AFO in heated soybean oil to AFF in French fries varies greatly among individual aldehydes. In general, the aldehydes containing 9–11 carbons had much greater AFF/AFO ratios than the aldehydes with 7–8 carbons. Overall, results from current study suggested that the interactions between aldehydes and food matrix may occur during frying and can contribute to the differences between the profile of AFF and the profile of AFO.

5. **Development of Novel Free-flowing Fish Oil-loaded Hollow Solid Lipid Micro- and Nanoparticles to Improve Oxidative Stability of Fish Oil.** Junsi Yang and Ozan N. Ciftci, *University of Nebraska-Lincoln, USA*

Effectively incorporating fish oil into foods and beverages is a major challenge due to its poor water solubility and sensitivity to oxidation during processing and storage. Therefore, the objective of this study was to develop a novel free-flowing powder fish oil formulation that can be added into foods and can protect fish oil from oxidation.

Fish oil was loaded into a solid lipid (fully hydrogenated soybean oil) using a single step process based on atomization of a CO_2-expanded lipid mixture. Fish oil-loaded hollow solid lipid particles ($d_{50\%}$= 5.6 µm) were obtained using 50 µm nozzle diameter and 200 bar expansion pressure, with loading efficiencies up to 97%. All particles were spherical and dry free-flowing. Shell thickness of the hollow solid lipid particles increased with decreasing pressure. Moreover, fish oil-loaded spherical hollow solid lipid particles obtained at 10%, 20% and 30% initial fish oil concentrations improved the oxidative stability of the loaded fish oil compared to the crude fish oil ($p<0.05$). Increasing initial fish oil concentration above 40% increased the amount of surface oil. Nanoparticles were successfully separated from microparticles by filtration, and formed clear liquid when added into water.

This simple and "green" method produces easy-to-use solid fish oil formulation in dry free-flowing powder form. The solid lipid shell protects fish oil from oxidative degradation and masks the fish smell, hollow structure provides high loading capacity, nanosize allows transparent beverage preparation, and the powder formulation makes handling and storage convenient.

6. **Physical and Oxidative Stability of 50-70% Fish Oil-in-Water Emulsions Stabilized with Sodium Caseinate and Phosphatidylcholine.** Betül Yesiltas[1], Ann-Dorit Moltke Sørensen[2], Pedro J. Garcia-Moreno[2], and Charlotte Jacobsen*[2], *[1]National Food Institute, Technical University of Denmark, Denmark; [2]Technical University of Denmark, Denmark*

This study aimed at optimizing the physical and oxidative stability of high fat omega-3 delivery fish oil-in-water emulsions stabilized with combinations of sodium caseinate (CAS) and phosphatidylcholine (PC). Combining PC as a surfactant together with CAS was expected to provide less viscous samples with improved physical stability as well as better oxidative stability due to additional antioxidant properties of PC. The influence of fish oil content (50, 60 and 70%, w/w), total amount of CAS and PC (1.4, 2.1

and 2.8%, w/w) and ratio between CAS and PC (0.4, 1.2 and 2) on physical and oxidative parameters were investigated.

Creaming and droplet size significantly decreased when the amount of fish oil, total emulsifier and ratio of CAS to PC were increased. Viscosity decreased significantly with decreasing fish oil content. However, no significant effect of variables was found on peroxide value, which was lower than 6 meq/kg oil in all emulsions. Volatile compounds were formed in low amounts (<50 ng/g in all emulsions) except for 1-penten-3-ol, which was in higher concentration in all emulsions (<150 ng / g). Decreasing the ratio of CAS to PC led to lower formation of 1-penten-3-ol, (E)-2-pentenal, (E)-2-hexenal and (E,E)-2,4-heptadienal, confirming antioxidative effects of PC. The experimental results were fitted to complete quadratic models and optimized by response surface methodology. An optimum recipe was found at 70% fish oil, 2.8% total amount of CAS and PC and 1.2 as the ratio of CAS to PC, which provided physical and oxidative stability.

7. **Identification and Quantification of Phytoprostanes and Phytofurans in Coffee and Cocoa By- and Co-products.** Mariana Ruesgas Ramon[1], Claire Vigor[2], Amandine Rocher[2], Guillaume Reversat[3], Joseph Vercauteren[3], Camille Oger[3], Jean-Marie Galano[3], Thierry Durand[3], Erwann Durand[4], and Maria Cruz Figueroa-Espinoza[5], *[1]SupAgro Montpellier, France; [2]Institut des Biomolécules Max Mousseron, France; [3]Institut des Biomolécules Max Mousseron, UMR 5247 CNRS, University of Montpellier, ENSCM, Faculty of Pharmacy., France; [4]CIRAD, France; [5]Montpellier SupAgro, UMR IATE, Montpellier, France*

Coffee pulp (CP), cocoa husk (CH) and cocoa pod husk (CPH), are the main by-products (CP, CH) and co-product (CPH) derived from green coffee and cocoa transformation. These wastes represent a non-expensive source of interesting biomolecules. Phytoprostanes (PhytoPs) derived from peroxidation of α-linolenic acid (C18:3 n-3, ALA) are biomarkers of oxidative stress in plants and humans and possess biological properties. Under high oxygen tension, phytofurans (PhytoFs) derived from ALA, were recently discovered in seeds, nuts, oils, and melon's leaves. There is a growing interest in the profile of these compounds in plant foods and their response to cultural, postharvest, and/or environmental conditions. The goal of this work was to identify and to quantify the PhytoPs and PhytoFs in the vegetal matrices, by micro-LC coupled to a QTRAP detector method. The content of PhytoPs and PhytoFs, found, were, respectively, of 663 and 543.1 (from CP), 438.8 and 278 (from CH), and, 149.8 and 393.7 (from CPH) ng/g dry basis (d.b.). 9-epi-9-F1t-PhytoP was the main PhytoP found in CP (171.4 ng/g d.b.) and CPH (37.1 ng/g d.b.), while ent-9-L1t-PhytoP was the main PhytoP in CH (109.8 ng/g d.b.). Additionally, ent-16(RS)-13-epi-ST-Δ14-9-PhytoF was the main PhytoF found in our samples (196.5, 126.2, and 207.6 ng/g d.b., from CP, CH, and CPH, respectively). This is the first time that a complete profile of these oxygenated lipids is realized in coffee and cocoa, showing the potential of plant biomass by- and co-products to be used as a source of these biomolecules.

8. **An Investigation of the Antioxidant Activity of Alkyl Gallates in Model Membranes.** Yu Zhao[1], Drew Marquardt[2], Ryan J. Elias[1], and John N. Coupland[1], *[1]Pennsylvania State University, USA; [2]University of Windsor, Canada*

Objective/Hypothesis: The objective of this study was to investigate the mechanisms of antioxidant activity (AA) of alkyl gallates (AG) with varying chain lengths in a model membrane system. We hypothesized AG with longer carbon chains would exhibit higher AA due to their higher affinities towards membranes and deeper penetration depths within those membranes. Methods used: The oxidation of aqueous liposome dispersions prepared from sunflower lecithin in the presence of 5 mol% AG was induced by water soluble radical initiator at 37 °C and followed with peroxide values. The physical locations of AG in liposome-water system were measured by ultracentrifuge, AG oxidative stability, NMR, fluorescence quenching and wide angle neutron diffraction (WAND). The effect of AG on membrane fluidity was measured by electron paramagnetic resonance (EPR). Results: The AA of AG increases with increasing chain length and the maximum activity was observed for decyl gallate. This result is corroborated with AG partitioning and oxidative stability studies. NMR results suggest a strong interaction between octyl gallates and phosphate group in lecithin. Fluorescence quenching suggests higher penetration depth of AG with longer chain and minimum distribution in membrane hydrophobic region. WAND shows both octyl gallate and palmityl gallate reside in membrane hydrophilic region. EPR shows AG cause no fluidity change in membrane. Conclusion: The maximum AA of AG series was observed for decyl gallate and AG is mainly localized at membrane hydrophilic region. This study provides an application of AG in treating age-related degenerative diseases and preventing oxidation in foods rich in polyunsaturated phospholipids.

9. **Predicting the Oxidative Stability in Bakery Products: Application of Accelerated Method Based on Oxygen Consumption.** Claudio Corradini[1], Antonella Cavazza[1], Emma Chiavaro[2], Carmen Lagana[3], Stefano Casiraghi*[4], Monia Scarsi[4], Maria Paciulli[5], Massimiliano Rinaldi[5], and Maria Grimaldi[6], *[1]Universita degli Studi di Parma, Italy; [2]Dipartimento di Scienze degli Alimenti e del Farmaco, Università di Parma, Italy; [3]VELP Scientifica, Italy; [4]VELP Scientific, Inc., USA; [5]Dipartimento di Scienze degli Alimenti e del Farmaco, Università di Parma, Italy; [6]Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Italy*

Bakery products are semi-perishable products with flour as main ingredient; they contain also fat, often in significant amount, that influences the softness, the flavor, the texture and the alveolation of the product [1]. For this reason, these products are particularly susceptible to lipid oxidation, that is considered the main cause of deterioration and causes the formation of off-odor and off-flavor compromising their acceptability. According to the product formulation, lipid oxidation depends on the nature of the fats or the presence of antioxidant molecules [2]. Traditional methods detected the oxidation stability by evaluating the quantity of primary and secondary products of oxidation. Accelerated methods are new analytical techniques based on the application of an oxidative stress: OXITEST is an innovative instrument used for oxidative stability studies of fat foods based on the monitoring of pressure of

a sample submitted to high O2 pressure and high temperature. In this work, oxidative stability was evaluated both on flours (with or without bran) and on cookies as well as on sponge cakes. Obtained results allowed distinguish between the different flours based on bran content, between cookies based on ingredient with antioxidant compounds and between palm and palm-free sponge cakes. In conclusion, OXITEST showed to be a suitable and affordable method for the study of oxidative stability of bakery products.

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10. **A Study of Photooxidation in Edible Oils by FTIR Spectroscopy and Incubation at Moderate Light Intensity.** Noelia Tena[1], Ramón Aparicio-Ruiz[1], Ana Lobo[2], María Teresa Morales[3], Aparicio Ramón[2], and Diego L. García González*[1], *[1]Instituto de la Grasa (CSIC), Spain; [2]Instituto de la Grasa (CSIC); [3]University of Seville, Spain*

Photooxidation process is less known that autoxidation and thermoxidation. However, it is one of the processes that causes that edible oils are oxidized in a short time, even in those crude oils with natural protection against oxidation. For that reason, gaining knowledge about the photooxidation of oils, in particular when low intensity of visible light is applied, is of high interest to understand how edible oils lose quality in the first months of storage and which chemical characteristics can promote or prevent the degradation process. With this purpose, mesh cell-FTIR has been applied to evaluate the combined effect of moderate light and temperature in the stability of different edible oils in mild conditions similar to those found in a supermarket. This strategy brings the advantage of highlighting small chemical changes at moderate conditions without the need of applying high temperature or light intensity to obtain observable changes. Thus, the results showed that moderate values of light intensity (400 lx) and temperature (23ºC) has an initial effect in the degradation of edible oils responsible for the quality decline. Thus, moderate light (400 lx) has proven to be a very important factor in the stability of lipid matrices, even in those oils that are known for being relatively more stable. Thus, a photoxidation study is shown to be a recommended action to determine the actual stability of edible oils in the programmed conditions of storage and to select the best packaging.

11. **Food-induced Formation of Health-damaging Compounds During Repeated Deep-fat Frying Cycles.** Ru Shen, William G. Helferich, and Nicki J. Engeseth, *University of Illinois at Urbana-Champaign, USA*

Repeat-utilization of frying oil, TAFO (thermally abused frying oil), results in undesirable compound formation; this is impacted by the fried food matrix. The overall goal of this research was to determine specific food-induced formation of undesirable components in TAFO. The central hypothesis was that undesirable compounds formed during repeat frying would differ based upon the foods fried. Frying experiments were conducted with 60 deep-fat frying cycles of chicken and fish in soybean oil with control oil heated separately without food. Oil and foods were periodically analyzed. For undesirable compounds, including EFA (epoxy fatty acids) and aldehydes in TAFO were characterized using GC and HPLC. Repeated

exposure to high-temperature frying led to significant deterioration of oil with increased total polar compounds (TPC: 4.35-11.93%). Control heated oils maintained quality (TPC: 2.86-3.10%). Chicken frying resulted in greater increase in TAFO free fatty acids. Fish resulted in a more dramatic increase in TAFO peroxide and p-Anisidine values than chicken. This result is consistent with oxidation product formation. TAFO accumulation of EFA was in the order of fish (145.01-451.36 µg/g oil)> chicken (152.34-543.32 µg/g oil) > control (104.89-163.80 µg/g oil). By contrast, EFA accumulation in fried food was greater in chicken (82.50-143.35 µg/g food) than fish (57.34-137.71 µg/g food). To conclude, frying oil deterioration was highly dependent upon the type of food fried. Fish frying contributed greater to oxidative instability whereas chicken contributed more to hydrolytic instability. Considerable accumulation of health-damaging undesirable compounds both in foods and oils during repeated deep-fat frying deserves more attention.

12. **Lecithin Near Critical Micelle Concentration had the Highest Oxidative Stability in Corn Oil.** JiSu Kim[1], YunSik Woo[1], Jiwon Ryu[1], MiJa Kim[2], and JaeHwan Lee*[3], *[1]Sungkyunkwan University, Republic of Korea; [2]Kangwon National University, Republic of Korea; [3]Dept. of Food Science and Biotechnology, Sungkyunkwan University, Republic of Korea*

Association colloids made of phospholipids and moisture are major places for the lipid oxidation. Depending on the experimental condition, antioxidative or prooxidative properties of phospholipids have been reported in the literature. The objective of this study was to determine the effects of lecithin (HLB 4.5) on the oxidative stability in corn oil at 50°C storage. The concentration of added lecithin was ranging from 300 to 3000 ppm, which could cover the critical micelle concentration (CMC) of lecithin in corn oil. The CMC of lecithin in corn oil was determined by tetracyanoquinodimethane (TCNQ) technique. Headspace oxygen content, conjugated dienoic acid (CDA), and p-anisidine value (p-AV) were analyzed for the oxidative properties and tocopherol content was also determined. Headspace oxygen content of lecithin-containing corn oil is reduced in a concentration-dependent manner, indicating the antioxidant properties of lecithin. Lecithin showed high oxidation stability by adding samples near CMC compared to others based on CDA and p-AV analysis. Tocopherols in oils containing near CMC of lecithin were detected in the highest concentration. Concentration of lecithin near or over CMC showed the better antioxidant properties than lower concentration of lecithin than CMC in corn oil. Therefore, it is recommended to control the contents of moisture and amphiphilic compounds near CMC to extend the shelf-life of bulk oils.

13. **Optimization and Validation of Rancimat Operational Parameters to Determine Walnut-oil Oxidative Stability.** Lucia Felix and Irwin R. Donis-Gonzalez, *University of California-Davis, USA*

Objective: The objective of this study was to optimize and validate the Rancimat (Metrohm Ltd., Herisau, Switzerland) operational parameters that minimize the coefficient of variation (CV) of walnut-oil oxidative stability (induction time) determination. This is a useful parameter to infer walnut rancidity potential and quality, after drying and during storage. In

addition, to better understand the relationship between walnut-oil hydrolytic rancidity and the lipid oxidation state, Free Fatty Acids (FFA) and hydro-peroxides, expressed by the Peroxide-Value (PV), were quantified each 15 min for 75 min, during Rancimat accelerated oxidation.

Methodology: Response Surface Methodology (RSM) using a Box-Behnken statistical design was used to optimize the Rancimat operational parameters (temperature, airflow, and oil sample weight). CDR FoodLab (CDR s.r.l, Florence, Italy), a system based on spectrophotometry was used to quantify FFA
and PV.

Results: Temperature, airflow, and oil sample weight equal to 125° C, 17 L-h $^{-1}$ and 2.5 g were the parameters that yielded the minimum induction time CV, equal to a mean ± standard deviation of 1.34 ± 0.25 from two triplicate replications. It was observed that FFA, and PV presence subsequently reached the highest level after 60, and 75 min induction time. Conclusions: In conclusion, RSM is a useful methodology to optimize Rancimat operational parameters, and minimize the CV in walnut-oil induction time determination. In addition, this study indicated that the Rancimat walnut-oil induction time is mainly influenced by the presence of volatile compounds (FFA), and it is not directly related to non-volatile oxidation products, as quantified by the PV.

14. **Correlation between Phenolic Compounds and Antioxidant Activity of Sapucaia Nut (Lecythis pisonis Cambess) Aqueous Extract.**

Fernanda Demolinder[1], Priscila Policarpi [2], Leticia Turcatto[2], Luciano Vitali[3], Gustavo A. Micke[3], and Jane Mara Block*[4], *[1]Dept. of Food Science and Technology—Federal University of Santa Catarina, Brazil; [2]Dept. of Food Science and Technology, Federal University of Santa Catarina, Brazil; [3]Dept. of Chemistry—Federal University of Santa Catarina, Brazil; [4]UFSC, Brazil*

Sapucaia (Lecythis pisonis Camb.) is a nut originating from the Brazilian Amazon region rich in essential fatty acids, protein, dietary fibers and minerals. Studies on sapucaia nut phenolic profile and antioxidant activity remain scarce in the literature. In this study the phenolic profile using the LC-ESI-MS/MS methodology, and the antioxidant capacity (Folin-Ciocalteu reducing capacity—FC, FRAP, and ABTS) of aqueous extract of sapucaia nut were determined. In the samples studied (from the states of Piauí and Minas Gerais) 14 phenolic compounds (7 phenolic acids, 6 flavonoids, and 1 phenolic aldehyde) were identified. The results showed a high antioxidant activity in the sapucaia nut extract: 34.15 to 48.13 µmol TEAC.g-1 in ABTS; 29.03 to 41.34 mg GAE.g-1 in FC; and 15.82 to 19.38 µmol TEAC.g-1 in FRAP. A significant correlation ($p < 0.05$) between the phenolic compounds and the FRAP and ABTS assays was observed ($r = 0.632$ and 0.854; 0.746 and 0.896; 0.665 and 0.846; 0.828 and 0.891, for ellagic acid, catechin, epicatechin and myricetin, respectively). A significant correlation ($p < 0.05$) between ferulic acid and the FC assay ($r = 0.628$) was determined. The results showed that sapucaia nut is a promising natural source of phenolic compounds exhibiting a high antioxidant activity. The data obtained in this work may be used to stimulate the local production and consumption of this type of nut, as well as its use for the food industry globally.

15. **Microwave-assisted Synthesis and Antioxidant Activity of Palmitoyl-epigallocatechin Gallate.** Tao Zhang, Ruijie Liu, Ming Chang, Qingzhe Jin, and Xingguo Wang, *Jiangnan University, China*

Objective: Palmitoty-epigallocatechin gallate (p-EGCG), a palmitic acid ester derivative of epigallocatechin gallate (EGCG), has been declared with strong bioavailability and bioactivity. In this study, synthesis of p-EGCG with microwave irradiation as well as its antioxidant activity was investigated.

Methods: p-EGCG synthesized by microwave irradiation was separated and purified by Medium Pressure Preparative Liquid Chromatography (MPLC). Quadrupole Time of Flight/Mass Spectrometry (Q-ToF/MS) was adopted for the identification of each fraction. Metrohm rancimat was utilized for the p-EGCG antioxidant activity evaluation in soybean oil.

Results: With the assistance of microwave irradiation, higher conversion rate (85.12%) was observed in a shorter reaction time (2 h) than that of conventional method. The major product was identified as p-EGCG with a purity of 91.73% after preparation by Medium Pressure Liquid Chromatography. Accelerated oxidation revealed that p-EGCG exerted stronger antioxidant activity than EGCG in the control of soybean oil oxidation. With an addition of p-EGCG (200 mg/kg), the shelf-life of soybean oil at 25 degrees was predicted to be 15.72 months.

Conclusion: These results obtained in this study revealed that p-EGCG may serve as a potential antioxidant and contribute to the preservation of edible oil or fat-based food.

16. **Comparison of Walnut Oil Obtained by Different Extraction Solvents.** Pan Gao and Xingguo Wang, *Jiangnan University, China*

The aim of this study is to select the best extraction solvent for walnut oil, and to guide the optimization of production to provide important quality control indicators. An analytical study on the oil yield, fatty acid and triacylglycerol composition, micronutrients content, oxidative stability and antioxidant capacity of walnut oils extracted by different extraction solvents (n-hexane, ethyl acetate, petroleum ether, acetone and subcritical butane) was conducted. Results showed that fatty acid and triacylglycerol compositions were little influenced by extraction solvent. Acetone was found to be the best extraction solvent for extracting walnut oil with best oxidative stability and antioxidant capacity when compared with other solvents. According to correlation analysis, squalene and total phenols were significantly positive correlated with OSI and four kinds of scavenging capacities (DPPH, FRAP, ABTS and ORAC), that are important indexes for evaluating walnut oil quality. This study contributes to the industrialized production of walnut oil, acetone to be used as extraction solvent for the potential of walnut oil production.

17. **Co-solvent Modified Supercritical Carbon Dioxide Extraction and Antioxidant Activity of Rosemary Extracts.** Ignacio Vieitez, Lucía Maceiras, and Iván Jachmanián, *UdelaR, Uruguay*

Supercritical fluid extraction with carbon dioxide (SC-CO2) has been demonstrated to be an attractive method to apply to the different processes involved in the food industry;

presenting several advantages compared with conventional organic solvents. Additionally, SC-CO2 solvent power can be modified by adding ethanol as a co-solvent at low concentrations to achieve extraction of both polar and non-polar compounds. In the present study, SC-CO2 extracts from Rosmarinus officinalis were obtained using different extraction conditions. Their antioxidant power in the protection of purified sunflower oil (p-SFO), stripped off from natural antioxidants, was determined and compared with that shown by different common synthetic antioxidants and with those obtained by traditional solvent maceration methods. Analysis were performed by adding the extracts or synthetic antioxidants to p-SFO at 500 ppm and the induction period (IP) of the oxidation process was determined by an accelerated oxidation method at 100ºC (Rancimat equipment). The IP of the p-SFO was 1.7 h, which increased 7.6, 8.3 or 31.5 fold by the addition of BHT, BHA or TBHQ, respectively. When the crude supercritical extracts from rosemary obtained at 50ºC and 300 or 400 bar using 10% of ethanol as co-solvent were added to p-SFO, the IP increased 10.8 or 15.2 fold, respectively. Results shown that supercritical extracts from rosemary were efficient for oil stabilization as much as the synthetic antioxidants tested; thus, they could represent a valuable natural alternative for the replacement of synthetic antioxidants.

18. **Opportunities for Low Saturate High Oleic Canola Oil in Food Industry: Frying Quality and Oxidative Stability.** Xiaolan Luo and Diliara Iassonova, *Cargill Inc., USA*

Clear Valley® Low Saturate canola oil developed by Cargill is the first canola oil with the lowest saturated fat on the market. It contains 4.5% or less saturated fat and has a high level of monounsaturated and a moderate level of polyunsaturated fatty acids. Compared to previous canola oil generations, it reduces 35% of saturated fat content while maintaining high frying and shelf life performance. The impact of saturated and monounsaturated fatty acid level on oxidative stability, flavor, and frying performance in the new canola oil was evaluated in comparison with commodity oils. The level of volatile organic compounds (VOCs) related to sensory was also evaluated. This new canola oil demonstrated high oxidative stability and favorable fried food flavor. Its superior frying performance and extended fry life help lower overall operation costs while delivering high-quality food with significantly reduced saturated fat content of fried products. Novel Low Saturate canola oil offers a healthier choice to customers for a wide range of applications.

20. **Radical Detection in Antioxidant Treated Fish Oil using Electron Paramagnetic Resonance.** Ewa Szajna-Fuller, Carrie Wray*, and Qing Bin, *Kemin Industries, USA*

The purpose of this study was to investigate radical species that are formed during autoxidation of PUFA-containing oils, such as fish oil, using electron paramagnetic resonance (EPR) spectroscopy employing spin traps. The effect of antioxidant molecules on the formation of radicals was also explored. The study was performed using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap. Fish oil was stored at 40ºC and periodically tested for presence of radicals by adding the spin trap at the time of testing. Several radical species have been observed in the fish oil as DMPO adducts, namely, peroxyl (LOO•), lipid alkoxyl (LO•), and lipid-based carbon centered (L•) radicals. Peroxide values and aldehydes were also monitored. Antioxidants, such as tocopherols,

carnosic acid, eugenol, and lutein, were added to the fish oil at 3 levels (50, 250, and 500 ppm) and a lower radical signal was observed in the presence of antioxidants.

21. **Effect of Temperatures on Thermal Oxidation of Oleic and Palmitic Acid Studied by ESR.** Hongjian Chen, Peirang Cao, and Yuanfa Liu, *Jiangnan University, China*

Objective High-oleic vegetable oils gain more concerns for their high frying stability, which constitute oleic acid from 75 to 90% and palmitic acid from 5 to 20%. However, thermal oxidation could also be induced for high-oleic oils during commercial frying process. This study is focused on thermal oxidation of oleic and palmitic acid at high temperatures.

Methods Used: Electron spin resonance (ESR) with dimethyl pyridine N-oxide (DMPO) as the spin trap was selected to study lipid-derived radicals. Hyperfine splitting constants and g values were calculated by Xenon software. Volatile compounds were analyzed by SPME-GC-MS/MS.

Results: Alkyl, alkoxyl and DMPO oxidized adducts were identified in the experimental spectra for both acids. For oleic acid, total amount of spins detected at 140°C was three times higher than that at 135oC. Below 135oC, alkoxyl adducts were the main radical adducts, then percentage of alkyl adducts increased to 63.89%. Futhermore, 9-COOH and 8-COOH were the major hydroperoxides, and more unsaturated aldehydes formed effecting the flavour of fryings at 140°C. For palmitic acid, total amounts of spins kept at a low level below 175°C, then increased almost 9 times from 0.405 to 4.875 at 180°C. The percentage of alkyl adducts increased to 80% at 180oC with alkoxyl adducts being the major adducts below 175°C. The C-C linkages of palmitic acid between carbons 2 to 6 were easier to be oxidized at 180°C.

Conclusions: The results all implied that oxidation rate of oleic acid increased sharply at 140°C, and 180°C for that of palmitic acid.

22. **The Evaluation of Frying Oils.** Dongjin Yu*[1], Eunseok Jang[1], Minyoung Kim[1], Bongchan Kim[1], Yoonchang Kang[1], Jinsub Shin[2], and Hyeonhwa lee[2], *[1]Samyang Co., South Korea; [2]Samyang Corp., South Korea*

The evaluations of new product that is the Long-life frying oil (LF) during deep-fat frying have been investigated. The frying oils such as soybean oil (Sb), Rapeseed oil (RP) and the long-life frying oil were used to fry 120 chickens. According to the frying number, oils were used as experimental samples. To investigate the change of oil quality and oxidation stability during frying, oils were examined. The increased acid values of SB, RP and LF were 1.39, 1.33 and 1.20, respectively. The change of color, smoke point of LF was lower than SB and RP. AS the number of frying was increased, total polar compound% (TPM%) of SB, RP and LF were 13%, 12.5% and 9.5%.

23. **Effects of Phospholipid Hydrolysis on Hemoglobin-mediated Oxidation of Different Lipid Classes in Washed Fish Muscle** Na Li, Wenjing Zhang*, and Mark P. Richards*, University of Wisconsin-Madison, USA*

Objective: The objective was to assess the effect of phospholipase A2 (PLA2) on hemoglobin (Hb)-mediated lipid oxidation in washed cod muscle (WCM) containing high and low levels of endogenous free fatty acids (FFA).

Methods: PLA2 from pig pancreas and trout Hb were added at 3, [1]25 U /kg WCM and 10 µmol/kg WCM, respectively. Heme degradation, lipid classes, and lipid oxidation in WCM were measured during 2°C storage (pH 6.7). Lipid hydroperoxides (LOOH) and thiobarbituric acid reactive substances (TBARS) were used as markers of lipid oxidation. Total lipids were fractionated into neutral lipid (NL), FFA and polar lipid (PL) using aminopropyl silica. Phosphatidylcholine (PC), phosphatidyl-ethanolamine (PE) and FFA were quantified using densitometry relative to standards run on thin layer chromatography plates. LOOH in FFA, NL, and PL fractions were determined.

Results: PLA2 inhibited heme degradation and Hb-mediated lipid oxidation more effectively in WCM containing low FFA (WCM-L) compared to high FFA (WCM-H). Phospholipid hydrolysis based on FFA formation and depletion of PC and PE was greater in WCM-L compared to WCM-H. PLA2 decreased the content of PL-OOH in WCM-L.

Conclusion: Low initial FFA was required for effective inhibition of Hb-lipid oxidation by PLA2. The low initial FFA resulted in enhanced hydrolysis of PL during storage. The depletion of PL-OOH by PLA2 in WCM-L may contribute to the mechanism of antioxidant action by PLA2 since hemin released from Hb is noted to degrade PL-OOH to alkoxyl and peroxyl radicals that degrade heme and propagate lipid oxidation.