Lipid Oxidation and Quality Interest Area
Technical Program Abstracts

Table of Contents

The presenter is the first author or otherwise indicated with an asterisk (*).
Abstract content is printed as submitted.

LOQ 1a: Lipid Oxidation Evaluation by Sensory

Chairs: M. Peitz, Archer Daniels Midland Co., USA; and S. Ramnarain, DSM, USA

Odorant Synergy Effects as the Cause of Fishy Malodors in Algal Marine Oils. R. Marsili, Marsili Consulting Group, USA.

While oxidation reactions of docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA) are responsible for fishy off-flavors in marine oils, gas chromatography-olfactometry (GC-O) studies have failed to reveal which specific oxidation products are involved. Initial GC-MS-O studies of marine oils with fishy malodors revealed numerous oxidation products, but none individually were characterized as fishy. However, when all sample volatiles were captured together and then desorbed simultaneously in GC-O experiments, the fishy malodor was evident, indicating odorant synergy effects were responsible. A novel method was developed using an olfactometry detector as a fraction collector to trap various peaks in marine oil chromatograms. The nose cone of the olfactometry detector was replaced with a PDMS foam absorption tube at various times during GC analysis. Combinations of GC peaks were trapped on PDMS tubes, desorbed in a Gerstel thermal extractor (off-line), and sniffed. The combination of two analytes was found to cause fishy malodors: heptanal and (E,Z)-3,5-octadien-2-one. Purge-and-trap, solid phase microextraction (SPME), and headspace stir bar sorptive extraction (HSSE) sample preparation methods prior to GC-MS were investigated. All methods confirmed the combination of heptanal and (E,Z)-3,5-octadien-2-one as the cause of fishy odor.

The Value of Good Sensory Lab Practices: Is It Really as Costly as You Think? S. Kassner, DSM Nutritional Products, USA.

Utilizing human perception is the most direct and effective means available to quantify sensory-relevant product characteristics which may have implications for customer or consumer acceptance. This is accomplished through the use of human assessors to profile product characteristics. However, the quality of the results obtained from the use of human assessors depends to a large extent in the lab set-up, selection and training of panelists, method selection, and panel maintenance. Similar to traditional analytical labs, international and regional standards have been established to guide such conditions, termed Good Sensory Lab Practices. Unfortunately, many labs do not follow such standards, often citing resource constraints as a hurdle to implementation and opting instead for their interpretation of “rapid” test methods. While rapid tests have their place in the realm of product understanding, and indeed carry a lower resource burden relative to more disciplined sensory analyses, they are not without limitations that should be considered within the overall context of a study objective. It is important that developers apply the same cost-benefit analysis towards establishing appropriate sensory evaluations as they would towards establishing appropriate analytical evaluations.

Triangle Difference Sensory Testing to Determine Photooxidative Changes in Soymilk Shows Differences Before Chemical Analysis. L.M. Bianchi[1], S.E. Duncan[2], S.F. O'Keefe[2], D. Johnson[3], and J.R. Webster[2], [1]Radford University, USA, [2]Virginia Tech, USA, [3]Kraft Heinz Co., USA.

The objective of this study was to determine how long HDPE packaging treatments with light protective additives (LPA) could protect soymilk from photooxidation as determined by sensory and chemical analysis. High-density polyethylene (HDPE) with titanium dioxide (TiO2) is often used to package dairy milk to protect it from effects of photooxidation. Soymilk was chosen to test three different HDPE packaging treatments containing low, med, and high LPA [TiO_2]). Additionally, two controls were tested, a foil-wrapped, no light penetration control, and a translucent, full light penetration control. Soymilk was stored in the different packages in a lighted, refrigerated display case for up to 36 days. Packages were randomly assigned to be removed from the display case (average light intensity: 2200 lux; 4°C) for triangle difference sensory testing and chemical analyses on days 1, 4, 8, 15, 22, 29, and 36. Sensory testing demonstrated that the high LPA HDPE bottles protected the soymilk from oxidized flavor for 15 days. Chemical analysis demonstrated that the high LPA HDPE bottles protected the soymilk from riboflavin degradation and oxidative end products for 29 days. Sensory testing was able to detect changes in the soymilk two weeks before chemical analysis showed significant changes.

Sensometrics and Chemometrics: Past, Present, Future. E.P.P.A. Derks, DSM Resolve, The Netherlands.

Sensometrics and Chemometrics are two different fields of research which developed separately in specific application areas and mostly in different scientific communities. Both disciplines are typically getting more in touch over the years, i.e. linking sensory to analytics, which raises the question what they have in common and how they differ. This presentation aims to provide an overview of past, present and future challenges for both disciplines. Sensometrics developed from psychophysics, sensory and consumer (market) sciences whereas Chemometrics developed as a disciple for multivariate data processing and modeling with a focus to the Analytical Sciences and later to Biochemistry. Especially the food and pharmaceutical industries show a growing number of so-called *omics applications. Analytical profiles from chromatography or spectroscopy are correlated to sensory phenotype variables (like taste, odour, appearance, etc.). The challenges in such studies are in analytical data processing (alignment, clustering) and multivariate modeling and model validation (i.e. assessment

of predictive ability). Other challenges are in the organization of multi-block models that combine multiple analytical platforms to assess their predictive ability of sensory phenotype variables. Another aim is in using the known sensory data structure (for example from discrimination tests) or prior knowledge in the definition of the multivariate models to make the results more plausible or to improve interpretation. With clear examples it will be outlined how both disciplines have profited, and continue to do so, from mutual cross-over.

LOQ 1b: Lipid Oxidation in Processed Foods, Industrial Applications, and Complex Matrices

Chairs: M. Hu, DuPont Nutrition & Health, USA; E. Craft, DSM, USA; and X. Tian, Kalsec Inc., USA

Use of Natural Antioxidants to Prevent Oxidation in Pet Food. F.M. Salaun[1], N. Coneggo[2], and L. Le Paih[1], [1]Videka Diana Pet Food, France, [2]DIANA Pet Food, USA.

Natural mixed tocopherols are widely used to protect oils and fats in pet food industry. However, the demand for alternative natural antioxidants is increasing as classical solutions available on the market place have limited efficacy compared to synthetic solutions.

Experimental designs are performed in order to determine the antioxidant efficacy of natural extracts and their potential synergism in kibbles or in bulk fats used in pet food industry (animal fat or sunflower oil). The antioxidant efficiency is evaluated by using complementary methods such as peroxide value, hexanal, Rancimat for fats, or Oxipres for kibbles.

In fats or kibbles, natural antioxidants have a positive action to delay lipid oxidation. Increased oxidative stability can be achieved, compared to usual synthetic antioxidant combination of BHA and propyl gallate. Depending on the nature of fat or kibbles, different performances of natural antioxidants composition are obtained. The design of experiment help to determine the best combination of natural extracts (e.g. green tea extract, rosemary extract, and natural mixed tocopherols). Dose effect of compounds is often not linear. The optimal amount of natural antioxidants is determined thanks to the study.

There is no universal solution to protect fats or kibbles against oxidation. Blends of natural extracts have to be selected based on the product profile.

Shelf-life Extension of Commercial Cooking Oils Through Natural Approaches. T.K. Yang and Y.P. Zou*, Wilmar (Shanghai) Biotechnology Research & Development Center Co., Ltd., China.

The shelf-life of commercial cooking oils was extended by natural approaches. The advantages and disadvantages were reviewed for commercial application of different natural antioxidation in cooking oils.

Impact of Reducing and Non-reducing Sugars on Lipid Oxidation in Low Moisture Baked Goods. S.A. Vieira and E.A. Decker, University of Massachusetts Amherst, USA.

Low-moisture snack foods are among the top contributors of saturated fat in the American diet. In this study, we determined the effect of reducing and non-reducing sugars at 0 to 0.342moles/kg on lipid oxidation in a model cookie system. The impact of glucose concentration on lipid oxidation was monitored by lipid hydroperoxides and headspace hexanal during storage at 55°C. Low concentrations of glucose (<.005) increased lipid oxidation rates while high concentrations (>.008) were antioxidant. Atequal molar concentrations, reducing sugars (glucose, fructose, and maltose) inhibited lipid oxidation, greater than two months increase in lag phase compared to the control. Sucrose inhibited lipid oxidation, but to a much lesser extent than reducing sugars. Confocal microscopy using Bodipy 493 as a fat soluble dye showed that the fat formed a continuous phase surrounding the starch granules regardless of sugar type. Reducing sugars may exhibit this effect due to their ability to act as a hydrogen donor which could inactivate free radicals or due to the production of Maillard reaction products (MRPs). For example, the l-values were lower and b-values were higher for cookies with non-reducing sugars compared to cookies with sucrose indicating that there were more MRPs. These results could be utilized to develop effective antioxidant strategies to extend shelf-life of low moisture baked goods.

Storage Stability of Roasted Nuts and Stabilization Strategy Using Natural Antioxidants. X. Tian, L. Burroughs, and N. Yang, Kalsec Inc., USA.

Nut has been a big player in the snack category and in recent year begins to penetrate into other product sectors such as bars, confectionery and bakery. While tasty and nutritious, nuts are vulnerable to oxidation due to their high oil content, and consequently affect the stability of nut containing products. Extensive studies on the stability of various nuts including peanuts, cashew, pumpkin seeds, hazelnuts, and almonds were conducted. Nuts were dry roasted and exposed to stressful conditions, being either exposed to light or stored at elevated temperature (40°C). Stability was monitored by measuring volatile oxidation products. Results showed that nuts stability varies a lot; they also responded differently to different storage conditions. Stabilization strategy of nut products will also be discussed. The effects of natural antioxidants such as rosemary, green tea, and tocopherols on the stability of nuts were investigated. Results showed that antioxidants efficacy is matrix dependent, in another word, there is no Panacea for all nuts. Method of addition is a critical factor affecting the efficacy of antioxidants, along with storage condition and product forms. Our studies will provide valuable information to nut suppliers and consumer products companies to improve the stability of nuts and nut containing products.

LOQ 2a: Metabolic Fate of Lipid Oxidation Products and Antioxidants in Foods or Biological Systems

Chairs: K. Miyashita, Hokkaido University, Japan; and S. Witeof, Cargill Inc., USA

Antioxidant Potential of an Olive Leaf Extract Component, Oleuropein, and Its Preventive Effect on Type 2 Diabetes. A. Umeno, K. Murotomi, Y. Nakajima, and Y. Yoshida, Advanced Industrial Science & Technology, Japan.

Olive leaf has great potential as a natural antioxidant, since it contains oleuropein and hydroxytyrosol as the major phenolic components. We studied the radical-scavenging activity of antioxidants by investigating the probe decay by peroxyl radicals and oxidative stress markers derived from linoleates. We evaluated the antioxidative effects of oleuropein and hydroxytyrosol in comparison with those of homovanillic alcohol by using fluorescein and pyrogallol red. It was found that the stoichiometric number of oleuropein and hydroxytyrosol was twice of that of vitamin E, mimicking Trolox and leading to the marked suppression of the oxidation of methyl linoleate micelles compared with Trolox. Therefore, we investigated the preventive effect of oleuropein against Type 2 diabetes (T2D) in Tsumura Suzuki Obese Diabetes (TSOD) mice, by measuring the plasma levels of hydroxyoctadecadienoic acids (HODEs). It was found that young TSOD mice were exposed to oxidative stress before the development of diabetic phenotypes, and fed an oleuropein-rich diet, which suppressed oxidative stress and T2D development. The results of human studies suggested that singlet oxygen participated in the development of T2D. These studies investigated 10and12(Z,E)HODE, which are specific biomarkers of singlet oxygen. In conclusion, oleuropein possesses antioxidative properties and prevents T2D.

In Search of Natural Phenolics or Derivatives with Potential Mitochondria Targeting Activity. C. Bayrasy[1], J. Lecomte[1], R. Upasani[2], B. Chabi[3], B. Baréa[1], E. Durand[1], C. Bourlieu[1], M. Clarke[2], D. Moore[2], C. Wrutniak-Cabello[3], and P. Villeneuve*[1], [1]CIRAD, UMR IATE, France, [2]GlaxoSmithKline, USA, [3]INRA, UMR DMEM, France.

The number of antioxidants that have been claimed to be potentially used in pharmaceutical or cosmetic sectors is very large. For example, thousands of phenolic molecules have already been structurally characterized and many of them have been evaluated in vitro for their radical scavenging or metal chelating properties. In front of this multitude of compounds, there is a need in evaluating their activity in cells and also a great interest in identifying specific molecules with mitochondria targeting activity to combat oxidative stress situations. In that context, we have screened several natural phenolic compounds or synthesized derivatives for their ability to scavenge ROS in fibroblast cells. For this, ROS inhibiting action was evaluated at short and long times. Our results showed that some molecules were active rapidly but lose their activity for longer term, while others tend to be more active at longer period. These results suggest that more detailed kinetics of ROS inhibiting action are needed for the most active compounds and that combination of fast and slow acting molecules are promising strategies to identify synergistic antioxidant combinations. Finally, the most promising candidates were evaluated for their mitochondria targeting activity, and among them, sinapine extracted from canola meal.

Oxidative Deterioration of Fish Oils and Its Prevention. M. Uemura, A. Shibata, and K. Miyashita*, Hokkaido University, Japan.

Fish oil rich in eicosapentaenoic acid (EPA; 20:5n-3) and docosahexaenoic acid (DHA; 22:6n-3) are very easily oxidized to form undesirable flavors. We have found the higher quantities of acrolein (2-propenal) at the early stages of oxidation of fish oil triacylglycerol (TAG). The acrolein quickly increased, but afterward, it either did not change or slightly decreased. On the other hand, in the oxidation of linseed and soybean oil TAGs, propanal, pentane, and hexanal were detected as major volatiles, but a little acrolein was formed. Thus, acrolein may act as a key compound having a strong impact on flavor deterioration of fish oil, especially at early stage of the oxidation. We have also found that the acrolein formation in the fish oil could be effectively inhibited by the addition of sphingoid bases such as sphingosine and sphinganine with α-tocopherol. The study showed that antioxidant compounds would be formed by the reaction between the amine group of sphingoid bases and the carbonyl groups of acrolein in the early stage of fish oil oxidation.

The Presence and Type of Flavor Present in Fish Oil Supplements Interferes with *p*-anisidine Testing. J.C. Sullivan Ritter[1], S.M. Budge[2], and M. Reid[1], [1]Nature's Way Canada, Canada, [2]Dalhousie University, Canada.

Fish oil dietary supplements because of the many health benefits they provide. The high levels of EPA and DHA in these oils mean that they are prone to rapid oxidation. The main measures of oxidation in fish oil are peroxide value and *p*-anisdine value (AV). Unfortunately, AV cannot be used on flavoured oils because flavours interfere with the chemical reaction, resulting in inflated AV values. In this study we analyzed AV on fish oils with different flavours to see what effects they have. We found that different flavours cause different increases on AV.

Combination of Oil Soluble and Water Soluble Green Tea Extracts and Rosemary Extract in Delaying Oxidation in Mayonnaise. J. Randall, L. Ban, N. Patel, and W.D. Schroeder, Kemin Food Technologies, USA.

Food emulsions have both a high lipid content and a large interfacial region that make them prone to an increased rate of lipid oxidation. This study aims to provide clean label alternatives to synthetics, such as ethylenediaminetetraacetate (EDTA), to stabilize mayonnaise. The hypothesis is that oil-soluble green tea extract, water-soluble green tea extract, rosemary extract, or combinations of these ingredients would provide increased stability, comparable to EDTA treatment, because of the differences in their physical locations in this complex system. Design of Experiment (DOE) was performed to evaluate the interaction of the three components, with EDTA (positive control) and untreated (negative control). In addition to the DOE the effect of packaging was also investigated. Two different packaging methods are evaluated, 1 gallon food service containers and 8 ounce retail bottles. Samples are stored at ambient temperature and evaluated for primary and secondary oxidative byproducts and sensory acceptability over time.

This study is important for not only providing a clean label alternative, but also through DOE to provide insight in the interactions of ingredients and their structural features to enable them to act as targeted ingredients in a heterogeneous system.

LOQ 2b /ANA 2.1: Prediction of Oxidative Stability, Shelf-life, and Antioxidants Effects

This session developed in conjunction with the Analytical Division.
Chairs: H.S. Hwang, USDA, ARS, NCAUR, USA; S.L. Hansen, Cargill, USA; and S. Seegers, Bunge Oils Inc., USA

Quantitative Determination of Antioxidant Distributions in Emulsions: A Partial Solution to the Polar Paradox Problem. L.S. Romsted[1] and C. Bravo-Díaz[2], [1]Rutgers University, USA, [2]University of Vigo, Spain.

Finding a method for determining antioxidant distributions in emulsions has proved difficult. We have demonstrated that pseudophase kinetic models that work in homogeneous microemulsions also work kinetically stable emulsions. Our solution uses a hydrophobic arenediazonium ion probe that reacts with an antioxidant in the interfacial region of emulsions.

The approach works because the totalities of the oil, interfacial, and aqueous can conceptually be treated as separate reaction regions without considering emulsion droplet size, but only the total volumes of the oil, water, and interfacial regions. Because the diffusivities of the reactants in emulsions are near the diffusion-controlled limit, reactants remain in dynamic equilibrium in kinetically stable emulsions after bulk mixing and their concentrations in each region are constant regardless of droplet shape or size.

This talk includes: (a) the assumptions of the pseudophase kinetic model; (b) the properties of the arenediazonium ion probe; and (c) methods for monitoring the reaction. The results demonstrate that our chemical kinetic method provides a versatile and robust approach for determining the effect of emulsion properties on antioxidant distributions and provides a natural explanation for the "cut-off" effect, the drop in antioxidant efficiency with increasing alkyl chain length of a particular antioxidant.

Modified Ferrous Oxidation-xylenol Orange Method to Determine Peroxide Value of Highly Pigmented Oils. R.R. Abuzaytoun[1], S.L. Mackinnon[2], and S.M. Budge[1], [1]Dalhousie University, Canada, [2]National Research Council of Canada (NRC), Canada.

A ferrous oxidation-xylenol orange method (FOX) was modified to measure total peroxides in highly pigmented oils. In the original FOX method, oil hydroperoxides oxidize ferrous ions to ferric ions, which in turn bind to xylenol orange (XO) that has a maximum absorbance at 560nm. When applying the FOX method in this manner, pigments such as carotenoids, which have similar $?_{max}$, will interfere with the absorbance measurement. To solve this problem, a further step was introduced to separate the XO-complex from pigments. In this proposed FOX method, distilled water was added after the XO-complex was formed; the XO-complex was completely extracted into the aqueous layer leaving behind a highly pigmented organic layer. The absorbance of the aqueous layer was measured at 560nm and the lipid hydroperoxide content was determined using a cumene hydroperoxide standard calibration curve. For method validation, oxidized, un-pigmented fish oil was analyzed with both the proposed modified FOX method and AOCS official method for peroxide values. A correlation coefficient of 0.998 was obtained showing that the values determined using the two methods were equivalent. This modified spectrophotometric FOX method for hydroperoxide determination of highly pigmented oils, such as krill and sea cucumber viscera oil, is a valuable alternative to the presently available PV methods.

Comparison of Shelf-life Assessment with Hydroperoxides and Volatile Compounds. J. Liang, F. Niu, D. Lv, Y. Zhang, and Y.R. Jiang,* Wilmar (Shanghai) Biotechnology Research & Development Center Co., Ltd., China.

Vegetable oils are susceptible to oxidation because of high content of polyunsaturated fatty acids.

This may bring up unpleasant off-flavor, taste, losses in desirable color and nutritive value, and affect shelf-life consequently. Shelf-life prediction has long been investigated to give industry instruction of storage time. Hydroperoxieds and induction period by accelerated methods have often been used to estimate the shelf-life of oil products with Arrhenius plots. Unfortunately, these studies can hardly reflect the real shelf-life of the products because of complicated factors affect the real shelf-life. In this study, soybean oil, sunflower oil, and corn oil were selected to collect accelerated oxidation data. Hydroperoxies, p-Anisidine value, and several other volatile compounds (hexanal, 2-heptenal, 2-pentyl furan, and 2,4 decadienal) have been tested. The shelf-life was predicted by Arrhenius plots with hydroperoxides and volatile compounds. At the same time, a two-year storage experiment with the same bench of oils was also done to compare the validity of the shelf-life assessments with different indices. These results will be presented.

Rapid Determination of Fryer Oil Quality. M.K. Gupta, MG Edible Oil Consulting, USA.

Fryer oil deteriorates as frying process progresses. As a matter of fact, the oil starts undergoing oxidation as soon as it is heated for frying without doing the actual frying of any food.

Numerous oil quality parameters are measured and reported by various researchers to define the quality level of the oil in the fryer. Among those are FFA (free fatty acid), PV (peroxide value), anisidine value, oxidized fatty acids, polymerized triglycerides, color, viscosity, etc. The buzzword around the frying industry has been TPM (Total Polar Material) in the fryer oil. The pioneering group, DGF (Germany) first suggested that the oil in the fryer is unfit for human consumption. Various countries have followed the

suit and have set their own guidelines for TPM, and some for FFA, to determine the end point of frying oil quality.

In our work, we measured soap by the AOCS Method (Cc-17-95 (09)) and measured TPM by AOCS Method (Cd-20-92 (09)) on oil samples from restaurant fryers and correlated the results. To our astonishment, we found a strong correlation between the two attributes. Therefore, soap in fryer oil can be used for rapid determination of TPM in fryer oil.

Method Development to Predict Frying Oil Stability by Treatment with Various Ingredients. L. Ban, J. Randall, N. Patel, and W.D. Schroeder, Kemin Food Technologies, USA.

This study aims at establishing methods to evaluate the impact of common ingredients on the improvement of frying oil stability, and comparing treated oils of lower stability with untreated oils of higher stability.

Frying oil stability is one of the crucial factors for the quality of both fried goods and oils. A common strategy is to use ingredients that can improve the oxidative stability. However, as frying studies are resource and time intensive, there has not been a study yet that incorporated a large number of ingredients and evaluated their interactions under real frying conditions. A previously developed high-throughput mini-frying method is combined with Design of Experiment to correlate the performance with the combination of ingredients. The variables contained more than 15 ingredients and their combinations were subject to frying in representative commodity oils, high oleic vegetable oils, and partially hydrogenated oils (PHO). The responses included total polar compounds and the production of toxic chemicals like 4-hydroxynonenal. The correlation will be able to aid the investigation to find PHO replacements without compromising oil stability. More importantly, this study will be able to help increase the value of less stable commodity oils which represent the most widely used oils worldwide.

LOQ 3a: Advances in Lipid Oxidation and Antioxidants—Fundamentals and Applications

Chairs: S. Bis, Kemin Industries Inc., USA; and F. Shahidi, Memorial University of Newfoundland, Canada

Antioxidants, Oxidation Control, and Impact on Food Quality. F. Shahidi, Dept. of Biochemistry, Memorial University of Newfoundland, Canada.

Antioxidants play a pivotal role in controlling oxidation via their participation in scavenging of free radicals by hydrogen donation and electron donation and via chelation of prooxidant metal ions. However, when included in different formulations, subjected to processing or ingested, changes are expected to occur in the efficacy of antioxidants in source materials or as added constituents. Thus, the quality of food is affected by both the nature and concentration of oxidation products as well as those of the antioxidants.

Therefore, presence of metal ions, food matrix constituents and formulations, storage and process conditions must be carefully considered along with the role structural features of antioxidants present in source materials. The importance of the content of soluble versus insoluble-bound antioxidants is another factor that deserves special attention. The presentation will provide an account of variables and factors affecting antioxidant efficacy, oxidation control and food quality.

Antioxidant Preservation of Meat Slurry for Pet Food. S. Cutler, Kemin Industries, USA.

Past work indicated that condition of the protein used in the pet food diet impacts shelf life stability of the diet. Fresh salmon, whitefish, or chicken slurry was treated with antioxidant formulations and held at refrigerated or frozen temperatures and tested for peroxide value.

Untreated whitefish slurry oxidized rapidly at both storage temperatures, reaching the maximum peroxide value by day 1 at 4°C and week 3 at -20°C. Treatment with a rosemary and tocopherol blend (product 1) controlled oxidation for 5 days at 4°C and for 3 months at -20°C. Salmon slurry showed improved stability at both temperatures with a higher rosemary antioxidant blend (product 2). Chicken slurry was slower to oxidize than the fish products but the PV generation rate was reduced by 4 fold when treated with product 1.

Chicken slurry treated with product 1 or untreated was used in an extrusion trial to confirm treatment raw material impacts diet stability. Kibbles made with untreated meat slurry did indeed generate PV more rapidly than kibbles made with antioxidant preserved slurry.

Results indicate the importance of treating protein raw materials with antioxidant to improve shelf life of pet food diets.

Controlling Lipid Oxidation in Oil-in-Water Emulsions with Polyphenol Coated Active Packaging Films. M.J. Roman[1], ***(Honored Student Award Winner, The Manuchehr Eijadi Award Winner, and Ralph H. Potts Memorial Fellowship Award Winner)***, E.A. Decker[1,2], and J.M. Goddard[1], [1]Dept. of Food Science, University of Massachusetts Amherst, USA, [2]Bioactive Natural Products Research Group, Dept. of Biochemistry, King Abdulaziz University, Saudi Arabia.

Metal promoted lipid oxidation decreases quality and shelf life packaged food products. Traditionally, synthetic metal chelators, such as ethylenediaminetetraacetic acid (EDTA), are added to stabilize these products. With increasing consumer demand for 'clean' label products, there has been interest in alternative preservation strategies. The objective of this research was to develop a polyphenol coated active packaging film to inhibit lipid oxidation in oil-in-water emulsions. The polyphenol coating was applied by *in situ* polymerization of catechol and catechin with laccase onto a chitosan-grafted polypropylene film. Polyphenol coated films demonstrated oxygen radical scavenging capacity (3.51±0.77nmol Trolox eq. cm^{-2}) and trolox equivalent antioxidant capacity (10.8 ± 0.77nmol Trolox eq. cm^{-2}). Iron chelating activity of polyphenol coated films was demonstrated at pH 4.0 (40.5±6.1nmol Fe^{2+} cm^{-2}; 32.3±3.3nmol Fe^{3+} cm^{-2}). Polyphenol coated films delayed the onset of lipid oxidation in soybean oil-in-water emulsions at pH 4.0. Such active packaging technology is a promising alternative to reduce synthetic additives and maintain quality of packaged food products.

Effects of Ferrous Iron, Blends of Tocopherol and Rosemary Extract, as well as Fruit Extracts on Oxidative Stability of Extruded Low Moisture Foods. M. Hu, DuPont Nutrition & Health, USA.

It is well documented that ferrous iron is a pro-oxidant that can initiate and accelerate lipid oxidation in bulk oil and food emulsions. How about the case of ferrous iron in the extruded low moisture human and pet foods? Fruit extracts like grape seed extract may work well as antioxidant in o/w emulsions, meat and meat products. Are fruit extracts effective as antioxidant in extruded dry pet food compared to the blends of tocopherol and rosemary extract? Is uncoated kibble matrix oxidatively stable? A research article reported that ferrous iron is an antioxidant in an extruded low moisture food. Our experimental result indicates that higher level of iron sulfate in the extruded kibble matrix may be an antioxidant, or at least may not be a pro-oxidant, based on PV and hexanal concentration changes over storage. Fruit

extracts such as grape seed, pomegranate and pine park extract did not work well in the coated chicken fat. However, the blends of tocopherol and rosemary extract were more efficacious than fruit extracts to increase the oxidative stability and extend shelf life of extruded dry pet food. Because kibble matrix is easily oxidized, antioxidants may be needed to add to kibble matrix to increase the oxidative stability and shelf life of extruded low moisture pet food.

LOQ 3b: Frying Oils—Applications, Quality, and Chemistry

Chairs: R.A. Della Porta, Frito-Lay, Inc., USA; J.K. Winkler-Moser, USDA, ARS, NCAUR, USA; and D.R. Johnson, University of Massachusetts Amherst, USA

Stabilizing Frying Oils—What Are We Missing? X. Tian and J.G. Redwine, Kalsec Inc., USA.

As simple of a cooking method as it appears, frying is a highly complex process where numerous physical and chemical changes take place. There are a number of factors affecting frying oil degradation, and it is a common practice in food industry to add antioxidants to increase stability, with the intention to replicate the success demonstrating significant stabilization of oil at room or moderate temperature. Unfortunately, these efforts have not always been successful. With an attempt to locate reasons behind these failures, major differences between oxidation at high and moderate temperatures will be reviewed. Also, new pieces of evidence that diverge from the traditional understanding of frying chemistry will be provided and discussed. Based on our accumulated data from frying studies, the levels of endogenous antioxidants in oils, the stability of added antioxidants at high temperature, and the methods selected to evaluate oil and food quality needs are some of the most critical considerations when developing stabilization strategy using antioxidant systems.

Amino Acids as Antioxidants for Frying Oil. H.S. Hwang and J.K. Winkler-Moser, USDA, ARS, NCAUR, USA.

Amino acids, proteins, and hydrolysates of proteins have been known to protect edible oils from oxidation. While amino acids and related materials have high potential as antioxidants for frying oil, effectiveness of each amino acid, and mechanisms of their activities are not well understood yet. Proposed mechanisms for antioxidant activities of amino acids include their radical scavenging abilities, regeneration of oxidized primary antioxidants, chelation of metals, and antioxidant activities of Maillard reaction products between amino acids and sugars or oxidation products. For better understanding on antioxidant activities of amino acids at frying temperatures, 21 amino acids were evaluated in stripped and un-stripped soybean oil at 180°C and correlations between molecular structures and antioxidant activities of these amino acids were examined. Some amino acids showed strong antioxidant activities. It was also found that antioxidant activities of amino acids largely rely on the synergistic effect with tocopherols.

The Role of Hydrophilic Antioxidants on the Chemical Stability of Algae Oil Organogel. B.C. Chen[1] and E.A. Decker[2], [1]North Dakota State University, USA, [2]University of Massachusetts Amherst, USA.

Lipid oxidation limits the utilization of long-chain n-3 polyunsaturated fatty acids (LC-PUFA) as nutritional supplements in processed foods. In this study, algae oil organogel was developed using monoglyceride (MAG). The physical properties of algae oil organgel, including rheology, thermal behavior and morphology were investigated. The impact of water content (5, 10, 20wt %) and MAG concentration (5, 10, 20wt%) the oxidative stability of fresh algae oil (i.e., refined algae oil without extra antioxidants) organogel was investigated by measuring the primary lipid hydroperoxides and secondary propanal lipid oxidative products during storage time at 45°C. In the addition, the antioxidative ability of hydrophilic antioxidants (grape seeds extract and ascorbic acid) on the oxidative stability of organogel in the presence and absence of water was also studied. The results showed GTE had the greatest protective effect against algae organogel oxidation and generated eight days lag phase, whereas ascorbic acid contributed to four days lag phase. The addition of 5wt % water shortened the lag phase of above system, being four and three days for GTE and ascorbic acid, respectively. The results from this study could provide information to build up stable food products containing high proportions of LC-PUFA.

Influence of Charged Surface-active Compounds on Lipid Oxidation in Oils Containing Association Colloids. R. Homma[1,2], E.A. Decker[2], and D.J. McClements[2], [1]Kao Corp., Japan, [2]University of Massachusetts Amherst, USA.

Association colloids formed by surface active minor compounds play an important role in the oxidative stability of oils by influencing the activity of both prooxidants and antioxidants. Dioleoylphosphatidylcholine (DOPC), which exhibits a slightly negative charge in an oil-in-water emulsion system, formed association colloids and retarded the formation of both primary and secondary lipid oxidations in fatty acid ethyl esters. In this study, the impact of charged association colloids on lipid oxidation in fatty acid ethyl esters was further investigated. Association colloids consisting of the anionic surface-active compound dodecyl sulfosuccinate sodium salt (AOT), cationic surface-active compound hexadecyltrimethylammonium bromide (CTAB), and nonionic surface-active compound 4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol (Triton X-100) retarded, promoted, and had no effect on lipid oxidation rates, respectively. Understanding how charged association colloids impact on lipid oxidation in oils could identify new food additives that would improve oxidative stability in oils.

LOQ 4a: Stabilization of Omega-3, Bioactive Lipids, and Antioxidants Strategies

Chairs: S.P.J.N. Senanayake, CFS North America, LLC, USA; and G. Yang, Kellogg, USA

Stabilization of Omega-3 Lipids with Antioxidants.
S.P.J.N. Senanayake, CFS North America, LLC, USA.

Due to their unsaturated nature, omega-3 oils and omega-3 enriched foods are highly prone to lipid oxidation, which will lead to development of undesirable odors and off-flavors during storage. Lipid oxidation of omega-3 lipids is a major concern that often leads to loss of shelf-life, nutritional value and safety. Based on the literature reports, many attempts have been made to delay oxidative deterioration of omega-3 lipids by using natural and/or synthetic antioxidants. In this review, how omega-3 oils and omega-3 enriched foods can be stabilized with natural and synthetic antioxidants are presented.

Oxidation Studies Using Natural Antioxidants in Highly Polyunsaturated Oils Using PetroOXY. P. Adhikari, Cargill Asia Pacific Food Systems (Beijing) Co., Ltd., China.

PetroOXY is the new equipment to measure oxidation and the effect of antioxidants in the edible fats and oils. Four different kind of natural antioxidants (rosemary extract, tea extract, bayberry extract and olive leaf extract) were selected as antioxidants in highly poly unsaturated oils. Among the tested antioxidants, tea extract and olive leaf extract showed better performance than berry extract and rosemary extract depending on the concentration. To better understand antioxidant effect, PetroOXY was compared with oven test (PV, p-AV, and polar compound). Rosemary extract and bayberry extract at 50ppm showed similar induction time (1.2h) and tea extract and olive leaf extract (50ppm) showed similar induction time (2.1h). But depending on the concentration of each antioxidant, induction time is varies such as tea extract showed best performance at 100 and 250ppm however olive leaf extract showed best performance at 500ppm followed by tea extract and bayberry extract. Moreover, total oxygen consumption, and oxygen consumption rate of each anti-oxidant containing oils showed the effectiveness and efficient of each antioxidants.

Optimizing the Stabilization of Fish Oil with Various Polar and Non-polar Extracts. P.C. VanAlstyne, Kalsec, Inc., USA.

Fish oils have been the topic of conversation for many years relative to the role that omega-3 fatty acids play in striving for optimal health. While rosemary has been shown to help stabilize fish oil, many refiners still struggle with the issue of oxidation between raw material procurement and delivery to customers. Most oxidative intervention occurs during the step after processing, but before packaging. The balancing act is to find that level of protection that affords the most protection yet is cost effective. The purpose of this study was to try to determine where that balance point may be. Fish oils were treated with increasing levels of polar or non-polar extracts of various plant origin. The efficacy of each level of addition was plotted and a determination was made of a target range between the level of ineffectiveness and over saturation. Data collected to date shows that above 0.6% addition of rosemary by weight is does not provide protection at a level commensurate to the protection afforded. Continuing studies will focus on point of addition and the effect on the quality of the finished, refined oil.

The Impact of Oxygen Concentration on Lipid Oxidation in Fish Oil-in-Water Emulsions. D.R. Johnson[1] ***(Thomas H. Smouse Fellowship Award Winner)***, J. Gisder[1], and E.A. Decker[1,2], [1]University of Massachusetts Amherst, USA, [2]King Abdulaziz University, Saudi Arabia.

The oxygen content of food systems, whether dissolved or in the headspace, is one of the most important factors influencing the rate and extent of lipid oxidation. Research has shown that headspace oxygen levels below 2% of the atmosphere provide significant enhancement of stability with a surprising lack of data between 2.0% to 20.9% (saturated) oxygen. In the present work, the impact of <1%, 1-2%, 4%, 8%, 12%, and 20.9% headspace oxygen above a 1.0% fish oil-in-water emulsion on lipid oxidation kinetics was determined. Atmospheres were modified using nitrogen/oxygen gas blends. Headspace and dissolved oxygen concentrations were monitored, simultaneously and non-destructively, by O_2-sensitive fluorescent sensors stored at 32°C for 19 days. Lipid oxidation, as measured by PV and TBARS, was inhibited at atmospheric headspace conditions at 8% oxygen or less. However, extensive protection against lipid oxidation was only achieved when headspace atmospheres were less than 2% oxygen. The viability of ascorbic acid to scavenge oxygen in reduced-oxygen emulsions was also determined. Results also suggested that monitoring dissolved oxygen may serve as an alternative indicator for assessing oxidative susceptibility. The results of this study provide a reference for the extent of oxygen reduction required for the protection of oxidatively sensitive ingredients.

Physical Stability, Autoxidation, and Photosensitized Oxidation of Omega-3 Oils in Nanoemulsion Prepared with Natural and Synthetic Surfactants. S. Uluata[1,2], D.J. McClements[2,3], and E.A. Decker[2,3], [1]Inonu University, Turkey, [2]University of Massachusetts Amherst, USA, [3]King Abdulaziz University, Saudi Arabia.

Fish oil is an important source of the omega-3 fatty acids, docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA) and they are important for human health. In this study, two natural (lecithin and quillaja saponin) and two synthetic (Tween 80 and sodium dodecyl sulfate) surfactants were used to fabricate omega-3 nanoemulsion using high-pressure homogenization (microfluidization). Initially, all the nanoemulsions contained small (*d*>100nm) and anionic (?–

potential from -8 and –65mV) lipid droplets (pH 7). All nanoemulsions were relatively stable to salt addition (0 to 500mM NaCl, pH 7.0). The impact of surfactant type on lipid oxidation was determined in the presence and absence of the singlet oxygen photosensitizers, riboflavin and rose bengal. Riboflavin and rose bengal accelerated lipid oxidation when compare to samples without photosensitizers. Lipid hydroperoxide formation followed the order Tween 80>SDS>lecithin>quillaja saponin and, propanol formation followed the order lecithin>Tween 80> SDS>quillaja saponin at 37°C for autoxidation. The same order of oxidative stability was observed in the presence of photosensitize oxidation promoted by riboflavin. Quillaja saponin consistently produced the most oxidatively stable emulsions, which could be due to its high free radical scavenging capacity.

LOQ 4b: Trans Fat Replacement: Chemistry and Oxidative Stability, Applications

Chairs: P. Smith, Cargill R&D Centre Europe, Belgium; and W.M. Indrasena, DSM Nutritional Products, Canada

The Application of Modelling to Develop High Quality Trans-free Oil Blends with Good Oxidative Performance. P. Smith[1], S.A. Smith[2], A. Patsioura[3], and O. Vitrac[4], [1]Cargill R&D Centre Europe, Belgium, [2]Cargill Inc., USA, [3]AgroParisTech, France, [4]INRA, France.

There is a strong legislative pressure to remove trans fats from the diet and strong consumer pressure to reduce saturated fats for health reasons, as well as sustainability reasons in the case of palm oil. Therefore, novel blends are required that can achieve the same functionality, but which are based primarily on unsaturated triacylglycerols. Naturally these are less stable. Therefore, there is a need to create and optimise such systems. Synthetic antioxidants are generally undesired so there is a drive to develop optimised natural antioxidant blends. However, it may still be difficult to replicate the performance of the previous products. Therefore, optimisation of blending and blend control in order to deliver the correct blend for the correct application is needed. By the use of modelling, we have developed techniques that can enable the performance of blends to be predicted. By use of this model, optimised blends can be considered for each set of application conditions. Therefore, optimisation is possible.

In this presentation, we will consider the nature of oxidation, how it is affected by the different conditions, and how we can then use modelling to create optimised blends and fry under optimised conditions.

Measuring the Activity of Natural and Synthetic Antioxidants During Frying. C. Gertz, Maxfry GmbH, Germany.

Deep fat frying is a complex physic-chemical process that produces fried foods with desirable color, appearance, flavor and texture. A variety of natural and synthetic additives is available to improve the oil and the fried product. Important factors to consider are the heat and oxidative stability of the oil, which can be measured by different methodologies providing information on the degradation processes of the oil during heating and cooling. All standard methods for oxidation stability are not carried out at 170-180°C and assumed that thermal oxidative changes at 100°C or 130°C are not different from those under deep-frying conditions. In practice, one could not do without numerous cost-intensive deep-frying tests, however. For the laboratory testing purpose, a new procedure has been developed to simulate and monitor the thermo-oxidative structural changes of fats and oils at ambient temperatures, under accelerated conditions using 110°C and under elevated temperature usually used for frying. Additionally, the effectiveness of various stabilizing agents under these different conditions are tested to estimate their real impacts on the formation of oxidized and polymerized compounds.

Production of Toxic α,ß-unsaturated Aldehydes During Simulated Frying Episodes: Comparisons of Common Frying Oils with Novel High-stability Algal Oil Products. M. Grootveld[1], S. Moumtaz[1], P. Jansson[1], V. Ruiz-Rodado[1], and M. Edgar[2], [1]Leicester School of Pharmacy, De Montfort University, UK, [2]Dept. of Chemistry, University of Loughborough, UK.

Human consumption of cytotoxic/mutagenic lipid oxidation products (LOPs) generated in thermally-stressed polyunsaturate (PU)-rich culinary oils may give rise to deleterious health effects. Since monounstaurates (MUs) are much less susceptible to oxidation than PUs, we have explored the oxidative resistance of two high-stability MU-rich algal oils [1,2] during simulated frying practices.

These frying oils, together with a range of commonly-utilised ones, underwent laboratory-simulated shallow- and deep-frying episodes at 180°C; samples were collected at 0, 5, 10, 20, 30, 60 and 90min. (n=6 replicates per oil). Aldehydes therein were determined by high-resolution ^{1}H NMR analysis.

Substantially lower levels of aldehydes were formed in products [1] and [2], e.g., only 5-20% of the *trans*-2-alkenal, *trans,trans*-alka-2,4-dienal and 4-hydroxy-*trans*-2-alkenal concentrations generated in corn, sunflower and extra-virgin olive oils, when exposed to these frying processes ($p<10^{-7}$-10^{-2}). Little or no aldehydes were generated in these algal oils prior to the 20min. heating time-point.

MU-rich algal frying/cooking oils generate markedly lower levels of toxic α,ß-unsaturated aldehydes than PU-rich vegetable ones when exposed to frying episodes, and therefore offer health-friendly advantages.

[1] Thrive™; [2] AlgaWise™ culinary oils.

Effects of Colloids on Physicochemical Properties of Trans-free Non-dairy Pre-whipped Topping. Z. Meng, M. Qiu, and Y. Liu, Jiangnan University, China.

Currently, whipped cream which produced from partially hydrogenated oils (PHO) is the most common type in the market, which need to thaw the emulsion and whip. There is an obvious practical value to develop the trans-free non-dairy pre-whipped topping. Fully hydrogenated palm kernel oil (FHPKO) was used as the fat base to eliminate trans fats for the production of pre-whipped topping.
The effects of colloid on average fat globule size, viscosity,

overrun and texture of non-dairy pre-whipped topping were studied systematically. Sodium alginate (SA) is good for improving the texture and hydroxy properlene methyl cellulose (HPMC) can increase the overrun. Sodium caseinate (NaCas) can stabilize the emulsion, when the addition is 1.4%, the average fat globule size is the minimum, 321.85nm; the overrun is 3.37; the quality is the best. Whey protein concentrate (WPC) will lead to the formation of large fat globule, high viscosity, low overrun and interface stability; it is not suitable for non-dairy pre-whipped topping. Rheological properties showed that samples with smaller fat globule size had a higher G', G'' values, indicating their better qualities to resist collapse and more stable for these pre-whipped creams.

LOQ 5a: Lipid Oxidation and Antioxidants: System Modeling and Data Interpretations

Chairs: L.M. Barden, The Kraft Heinz Co., USA; and N. Yang, Kalsec Inc., USA

Modeling Physical Interactions in Oxidized Lipid Systems. D.A. Pink[1,2] and E. Papp-Szabo[1], [1]St. Francis Xavier University, Canada, [2]University of Guelph, Canada.

Solid fats and liquid oils play essential roles in oil binding capacity. Triacylglycerol molecules with unsaturated hydrocarbon chains can become oxidized, resulting in off-flavour and discoloration. Lipid oxidation can impact functionalities and have effects beyond rancidity. Phospholipid bilayers form the basis of biomembranes and lipid oxidation can affect their physical properties. Oxidation products can affect receptors and proteins, and influence signaling processes implicated in medical conditions. Although the chemistry of many lipid oxidation processes is known and their chemical pathways understood, the physical pathways and their outcomes are not necessarily clear: while the former involves a few molecules, the latter can involve cooperativity and larger scale diffusion. Modeling and computer simulation can help elucidate those physical pathways. We shall review models of oxidized lipids (eg Khandelia&Mouritsen Biophys.J, 96, 2734, 2009) and outline molecular dynamics and coarse-grained modeling techniques. The intent is to understand the physical consequences of oxidation with applications to (a) oxidized single-component oils and coated crystalline nanoplatelets, (b) plant-oil-based lubricants and (c) fat globules in milk. We shall illustrate some of the models with computer simulations, relate them to experimental data, and make predictions that might aid in developing new anti-oxidation strategies.

Modeling the Product Quality Impact of Oil Stability in Grain-based Snacks. M. Sewald[1,2], [1]Medallion Labs, USA, [2]General Mills, USA.

Analytical and sensory measurements of lipid oxidation are useful and practical means to gain insight in product quality. Predictive modeling tools based on these measurements can provide significant time and cost savings; allowing food companies to assess formulations and optimize logistics planning. This presentation reviews examples of applications for grain based snacks, with an over view of methods to develop and validate a basic quality model. These topics will be described at a relatively general level to provide a basic understanding for non-statisticians.

Methods for Optimizing Oxidative Shelf-life in Edible Oils. D.P. Barr, Bruker BioSpin, USA.

Rancidity of edible oils and lipids occurs by a free radical process due to exposure to elevated temperatures, light, and/or aging. Lipid-derived free radicals react further with oxygen to perpetuate radical chain reactions that result in carbonyl end products such as aldehydes and ketones. Antioxidants help to resist free radical oxidation. And although oxidation is inevitable over time, it can be minimized by optimizing production operations and storage conditions to provide maximum antioxidant content in the final product. The EPR forced oxidation profile provides an analytical measure for evaluating the overall antioxidant status of oil and lipids at each stage of the production process. The EPR data is also useful for predicting the shelf life of a final product before it goes through costly packaging and distribution. The sample is heated to 70°C to force its oxidation and a special reagent called a spin trap is added to capture free radicals as they form. Described here are two multi-purpose bench top EPR spectrometers (the e-scan and the EMXnano). The e-scan is interfaced with an automatic sample changer to provide EPR oxidation profile data for up to 20 samples all in one assay period. A typical assay is performed in a 1-3 hour period for 10 to 20 samples.

LOQ 5b: General Lipid Oxidation and Quality

Chairs: C. Hall, North Dakota State University, USA; and S. Nathan, Wilmar International Ltd., USA

Lipid Oxidation in Powder Matrices: A Critical Assessment of Peroxide Value. L. Smith, DSM Nutritional Products, USA.

Increased use of microencapsulated oils has made understanding lipid oxidation in the powder matrix very important, but more complex relative to neat oil systems. The objective of this study was to assess the utility of the industry standard peroxide value (PV) test as a determinant measure of primary oxidation in a powder matrix. The study was conducted with oils representing a range of peroxide values, which were subsequently formulated into a model dry form. PV results before and after formulation and oil extraction were compared. Data suggest that peroxide values are impacted by extraction technique, and alternative analytical techniques are needed in order to gain an accurate picture of the oxidative status of microencapsulated oils.

The Nonlinear Effect of Alkyl Chain Length of Phenolipids in the Membrane Interactions and Oxidation: Evidence by X-ray Diffraction Analysis. E. Durand[1], R.F. Jacob[2], S. Sherratt[2], J. Lecomte[1], B. Baréa[1], P. Villeneuve[1], and R.P. Mason[2,3], [1]CIRAD, UMR IATE, France, [2]Elucida Research, USA, [3]Dept. of Medicine, Cardiovascular Div., Brigham & Women's Hospital, Harvard Medical School, USA.

Phenolics represent a large family of secondary metabolites, ubiquitous in the plant kingdom and highly diversified. Although under native form they are effective antioxidants, their hydrophilic nature may be sometimes prejudicial to their antioxidant efficacy. Indeed, in complex systems such as emulsions, membranes, and living cells, it is generally considered advantageous for antioxidants to exhibit surface-active properties. One strategy to obtain surface-active phenolics consists in their association via covalent bond with a lipophilic moiety to design a new class of molecule called "phenolipids". As tailor-made new bioactive molecules, the phenolipids have proved to be a promising way to enhance their natural antioxidant property. This grafted lipophilic domain kinetically modulated the ability of the phenolipid to interact and cross cell membranes. Despite the evidence supporting a relationship between phenolipid's alkyl chain length and their interaction/affinity with membrane bilayer, such a relationship has not been directly visualized. In this study, the membrane interactions of rosmarinic acid, considered as one of the most efficient antioxidant, and its corresponding alkyl esters have been examined via small angle x-ray (SAXS) diffraction approach in model membrane liposomes and correlate with the overall peroxidation of the membrane.

Oxidative Stability of Oleogels Produced by Ethylcellulose and Monoglycerides. R. Homma[1], Z. Haizhen[1], S.M. Ghazani[2], A.G. Marangoni[2], D.J. McClements[1], and E.A. Decker[1], [1]University of Massachusetts Amherst, USA, [2]University of Guelph, Canada.

Oleogel research is focused on the development of an alternative triacylglyceride-structuring method using liquid oil and gelators instead of saturated fats and trans-fatty acids. However, replacing hard fats with liquid oil can change the oxidative stability. To understand the impact of gel structure on lipid oxidation, oxidation rates of gels and non-gels which contained the same gelators were studied. As a model of food system, three types of oleogels such as oil gels, water-in-oil gels, and oil-in-water gels are produced. First, oils with and without gelators were compared. The ethylcellulose gel structure did not affect lipid oxidation while the monoglycerides gel structure increased the oxidative stability of oil. Second, water-in-oil systems with and without gelators were tested. Both ethylcellulose and monoglycerides gel structure slightly increased oxidative stability of water-in-oil emulsion. Third, oil-in-water systems with and without gelators were studied. MAG gel structure increased oxidative stability of oil-in-water emulsion. The effects of antioxidants with different polarities on lipid oxidation in oil gels, water-in-oil gels, and oil-in-water gels were also studied. Understanding how gel structure impact on lipid oxidation could provide important information of how the gel systems could impact shelf-life and could provide a new perspective to improve oxidative stability.

GC-MS Characterization of Hydroxy Fatty Acids Derived from Oxidation of Edible Oils. W. Xia and S.M. Budge, Dalhousie University, Canada.

Lipid alcohols are thought to form from alkoxy radicals through hydrogen abstraction during lipid oxidation and are expected to be major intermediate products in addition to hydroperoxides. However, there are few applicable methods for their determination in oils. This is due to the poor sensitivity of the available methods and the limited knowledge of the structures of hydroxy fatty acids produced during lipid oxidation. Previous studies measuring hydroxy fatty acids utilized hydrogenation to optimize signals in GC-FID, which led to a loss of information regarding number and positions of double bonds. Here, we report a sensitive method to characterize hydroxy fatty acids in oxidized oils without hydrogenation. Triacylglycerols in oils were first converted into fatty acid methyl esters (FAMEs) using a base-catalyzed esterification method and then subjected to solid

phase extraction, where polar FAMEs including hydroxy FAMEs were separated from non-polar FAMEs. The hydroxy FAMEs were silylated before GC-MS analysis to form trimethylsilylated derivatives which showed characteristic peaks in mass spectra. This enabled structure elucidation and gave improved signal responses for quantification. Using this method, 6 hydroxy fatty acids were successfully identified in oxidized soybean oils, including those with conjugated double bonds.

LOQ-P: Lipid Oxidation and Quality Poster Session

Chair: X. Pan, DuPont Nutrition & Health, USA

1. **The Use of Factorial Design to Accelerate the Oxidation of Oils Containing Different Types of Omega-3 Fatty Acids.** T.A.D. Fabiano and I.A. Castro*, LADAF, Dept. of Food & Experimental Nutrition, University of São Paulo, Brazil.

In this study the action of five inductors and their binary interactions on four commercial oils oxidation was evaluated using a fractional factorial planning (2^{5-1}) ½ fraction with resolution V. Canola, flaxseed, echium and fish oils were chosen as the sources of omega 3 fatty acids: α-linolenic (ALA; C18:3 n3), stearidonic (SDA; C18:4 n3), eicosapentaenoic (EPA; C20:5 n3) and docosahexanoic (DHA; C22:6 n3). 10mL of each oil was mixed with $FeSO4.7H_2O$, 2,2,´-azobis (2-amidinopropane) dihydrochlororide (AAPH) 2,2´-azobis 2,4-dimethylvaleronitrile (AMVN) and ascorbyl palmitate and kept in an incubator at 30-50°C for 2 days. Hydroperoxides (LOOH) and TBARS concentration in oils were used as oxidative markers. Canola oil's preliminary results showed maximum values of LOOH and TBARS would be obtained by combining 2.0mMol $FeSO4.7H_2O$+0.81% AAPH + 1.00% AMVN at 50°C. Echium oil maximized values with a combination: 2.0mMol $FeSO4.7H_2O$+1% AAPH+0.85% AMVN at 42.7°C. Ascorbyl palmitate did not promote TBARS increase in both models. These preliminary results suggest that the inductors act differently depending on the type of omega 3 polyunsaturated fatty acid source and that factorial designs can be a useful tool to accelerate oils' oxidation by optimizingthe combination of several inductors.

2. **Effect of Water Activity, Solid Fat Content, and pH on Lipid Oxidation in a Model Crackers System.** T.P. Vu, L. He, D.J. McClements, and E.A. Decker, University of Massachusetts Amherst, USA.

Low moisture foods such as crackers and cookies, contribute to a large amount of saturated fats in the American diet. Because decreasing the consumption of saturated fats and increasing the consumption of polyunsaturated fats can help alleviate the risk for coronary heart disease, substituting saturated fats with polyunsaturated fats could have a positive impact on consumer health. However, this reformulation is challenging because polyunsaturated fats are more prone to lipid oxidation. The fundamental mechanisms of lipid oxidation in low moisture foods is not well understood. This study aims to better understand the influence of water activity (aw) and solid fat content (SFC) on lipid oxidation in a model crackers system. Aw of crackers (0.05, 0.1, 0.25, 0.4, and 0.9) was controlled by storing samples at different humidities. Interesterified and blended fats that had similar amount of linoleic acid but varied SFC were tested. Lipid oxidation was evaluated by measurement of lipid hydroperoxides and headspace hexanal. At aw=0.4, the lag phases of both hydroperoxides and hexanal were considerably longer than those of other aws. The impact of both aw and SFC was also determined.

4. **Effect of Genotype on the Oil Content and Fatty Acid Composition of the Oils from Sunflower Seeds Cultivated in Brazil.** R.D.A. Amaral, L.C. Rabonato, R.S. Oliveira, T.D. Alexandrini, and R.A. Ferrari, Food Technology Inst., Brazil.

Advances in oil seed biotechnology have enabled to produce genotypes with singular characteristics, as altered fatty acid compositions. Special interest has been done to high oleic content (more than 80% of this acid in sunflower oil) due its better oxidative stability and high quality of biodiesel produced. This work studied the oil content and some quality aspects of oil extracted from twenty-four different sunflower genotypes cultivated in Brazil. It was performed analysis of oil content, oxidative stability by Rancimat method at 100°C and fatty acid composition by GC. According to the results, the oil content varied from 18 to 57% and the oleic acid content varied from 29 to 90%. However, samples with higher oleic acid content do not present the higher oil content; in those samples this content represented 45%. Twenty-five percent of genotypes were classified as high-oleic due the oleic acid content above 80%. Furthermore, the content of this acid was directly proportional to oxidative stability. In conclusion, results indicated that sunflower genotypes cultivated in Brazil gave different results in oil content and fatty acid composition and these information are important for selection of genotype according to the purpose.

6. **Authentication of Turkish Extra Virgin Olive Oils Using a Portable Infrared Technology.** D.P. Aykas[1], A.D. Karaman[2], B. Keser[3], and L.E. Rodriguez-Saona[1], [1]Ohio State University, USA, [2]Adnan Menderes University, Turkey, [3]AYTB Lab., Turkey.

Olive oil is an economically important product and commonly adulterated with inexpensive oils to increase the profit. Additionally, oxidative stability of olive oil is an important characteristic due to its high oleic acid content. Current analytical characterization methods rely on chromatographic and titrimetric methods that are time-consuming, expensive, and labor-intensive. Our objective was to establish reliable authentication program for extra virgin olive oils (EVOOs) and assess the quality parameters using portable mid-infrared techniques combined with pattern recognition analysis. Samples (n=92) were provided by Borsa Laboratories, Aydin-Turkey. Fatty acid profile (GC-FAME), peroxide value, free fatty acids, pyropheophytins, 1,2-Diacylglycerols were evaluated using official reference methods. A portable ATR-IR with a temperature controlled (65°C) crystal was used to collect spectra and analyzed by soft

independent model of class analogy and partial least squares regression (PLSR). PLSR models showed good correlation coefficients (R^{2}≥0.92) between reference tests and FT-IR spectra, allowing for rapid determination of fatty acid composition and predicting oxidative stability. Oils formed distinct clusters allowing the evaluation of EVOOs from lower quality or adulterated oils. Portable FT-IR enables portability and ease-of-use, making it a great alternative to traditional methods.

8. **Oxidative Stability of Palm and Other Vegetable Oil Blends in Deep Fat Frying Applications.** C. Soriano and G.L. Baker, University of Florida, USA.

Unsaturated oils undergo hydrogenation to increase oxidative stability, extend shelf life, and provide mouthfeel similar to saturated fats. However partial hydrogenation can form *trans* fatty acids which have been associated with increased LDL cholesterol and risk for cardiovascular disease. With the recent ban of partially hydrogenated oils (PHOs), there is a need for alternative frying oils derived from natural fats. Binary oil blends were developed with palm oil (PO), palm olein (OL), or palm kernel oil (PK) and varying percentages of soybean (S) or canola (C) oil (0-100%). Blends were screened in triplicate using a modified Rancimat method measuring oxidative stability at 175°C to mimic changes at deep-fat frying temperatures. Results revealed 100% OL, 90/10 POC, 90/10 POS, and 90/10 PKC had the longest induction periods of 0.418, 0.397, 0.357, and 0.350h respectively, and therefore longest predicted fry-life. Blends comprising of PO≤0.50 had the shortest induction periods with a range of 0.083-0.110h, and PK blends with S≥0.50 had the shortest induction periods. These results present alternative frying oil matrices developed with goals of enhanced stability, flavor formation, and cost of production which may benefit the fried food industry.

9. **Do Glassware Washing Procedures Affect Oxidative Stability Index (OSI) Equipment Measurements?** L. Bueno-Borges, G. Santos, N. Sangaletti-Gerhard, and M. Regitano-d'Arce*, Luiz de Queiroz College of Agriculture, University of São Paulo, Brazil.

Resistance of oils towards oxidation can be determined by commercially available oxidative stability index (OSI) instruments. Although a very straight-forward analysis, cleaning the tubes and other components of the equipment is a difficulty known amongst oil analysts. The hypothesis of this work was to verify if glassware contamination by oil residues can alter measured conductivity levels, leading to erroneous results. Therefore, eight sets of glassware were divided into four groups of duplicates, each one corresponding to cleaning treatments to be applied after oxidative stability analysis using aliquots of the same oil as sample. Changes in induction period (IP) between the control (new glassware) and treatment groups were observed. The best treatment consisted of a combination of thorough cleaning with brushes, neutral detergent and tap water followed by hot bath with ethanolic 3% KOH solution for 4 hours, achieving an IP of 9.48±0.91 (hours) after 20 uses/washes of the glassware, also improving the initial IP presented by the control group (8.74±0.09). Other treatments showed the results of 8.95±0.74, 8.26±0.58 and 8.53±0.07. Results demonstrate that glassware cleaning highly influences OSI instrument measurements, and is a crucial step for ensuring reliable results.

10. **High Stability Soybean Oil Obtained from Ethanolic Extraction.** L. Bueno-Borges, G. Santos, N. Sangaletti-Gerhard, and M. Regitano-d'Arce*, Luiz de Queiroz College of Agriculture, University of São Paulo, Brazil.

The extraction of soybean oil using heated ethanol as solvent has been researched by our group for over a decade. Extraction results in an oil-rich miscella containing approximately 90% oil content, 7% ethanol, 0.4% phospholipids, 0.7% free fatty acids and 0.3% water. This work aimed to address the stability of this miscella in comparison to hexane-extracted degummed, neutralized and refined soybean oil. Samples were subjected to Oven Storage Test for 8 days at 62±1°C with Peroxide Value (PV) monitoring and analysis in an oxidative stability index equipment. Additionally, tocopherol content was determined by reverse-phase HPLC. All assays were performed in triplicate. The induction periods found for the samples were: 22.37±1.61; 7.94±0.24; 7.76±0.42; 6.65±0.21 hours for the miscella, degummed, neutralized and refined oil, respectively. After the eighth day of oven test, sample's PV showed a range of 1.33-4.23; 1.77-94.18; 1.24-89.51; 1.63-149.67meq/kg. As for the tocopherol contents, results were 283.7, 1023.2, 895.2 and 677.0mg/g sample. Differently from the other samples, the high stability showcased by the miscella was not related to tocopherol content. These results may be related to the extraction of compounds, other than tocopherol, with high affinity to ethanol, conferring significant resistance to oxidation to the miscella.

14. **Omega-3 Egg Yolk Fortification Using a Processing Approach.** S.Y. Gonzalez and J. Wu, University of Alberta, Canada.

The overall objective of this study was to enhance the oxidative tolerance of two types of fish oil by encapsulation within egg yolk (EY). Omega-3 triglycerides or ethyl esters were added at levels of 1 and 5% each (w/w) into EY; EY was used as control. The encapsulation was performed by homogenizing the samples in an Ultra Turrax. The particle size distribution (PSD) and oxidative stability of the fortified EY were investigated during storage over four weeks at 4-6°C. Light scattering was used to evaluate the PSD, and the peroxide value to assess the oxidative stability. A Randomized Complete Block Design with three replicas was used for the experimental design; data was subjected to one-way analysis of variance (ANOVA). EY containing 5% of omega-3

triglycerides had a significant larger particle size (P<0.05) than the rest of the samples and the control; however, the lack of significant differences on the PSD of each sample over time proved the particle stability. On the other hand, no peroxide content was detected for all samples after four weeks storage, thus showing the potential of EY as a suitable carrier to enhance the oxidative stability of omega-3 fatty acids.

18. **Novel, Natural, and Multifunctional Emulsion Stabilizers: Softwood Hemicelluloses.** M.J. Lehtonen[1], S. Teräslahti[1], M. Merinen[1], C. Xu[2], P. Kilpeläinen[3], A.M. Lampi[1], S. Willför[2], and K.S. Mikkonen[1], [1]Dept. of Food & Environmental Sciences, University of Helsinki, Finland, [2]Johan Gadolin Process Chemistry Centre, Lab. of Wood & Paper Chemistry, Åbo Akademi University, Finland, [3]Natural Resources Inst. Finland, Finland.

The interfacial characteristics of emulsions play an important role both in the maintenance of small droplets, i.e., large surface area, and in the interactions of the dispersed components with the surroundings. Thus, by varying the structure of the interface, the emulsion properties may be tailored. We studied the emulsion stabilization features of softwood hemicelluloses, spruce *O*-acetyl-galactoglucomannans (GGM). Stripped rapeseed oil-in-water emulsions (5wt.-% oil, 1wt.-% GGM) were prepared by high pressure homogenization using a microfluidizer. Physical and oxidative stabilities of the emulsions were followed during accelerated storage test at 40°C for over two months. The physical stability was characterized by droplet size distribution and oxidative state was evaluated by peroxide value, by volatile oxidation products (SPME-GC-MS), and by polymerized lipids (SEC-RI). Free and bound phenolic residues associated with GGM were determined from the interface and from the continuous phase to explain the stabilization mechanisms. GGM efficiently maintained the emulsion morphology and inhibited lipid oxidation. Changes occurring in the interfacial phenolic residues during storage explained the oxidative stability. Obtained results show that softwood hemicelluloses can be used as multifunctional stabilizers, for example, in food.

19. **Accelerated Oxidation Tests on Olive Oil Stored in Plastic Packaging and Submitted to Autoclaving.** S. Corti[1], S. Corno*[1], P. Salvadeo[2], C. Corradini[2], and S. Casiraghi[1], [1]Velp Scientifica srl, Italy, [2]Dept. of Chemistry, University of Parma, Italy.

Food packaging technology has undergone fast and significant developments in the past three decades, and the smartest are yet to be seen. Plastic materials can now be used for applications once restricted to metals and glass, allowing weight saving and design versatility benefits.
In this context, an important step to take into account during the production process is the resistance to autoclaving, a sterilization process at high pressure and temperature. Indeed an alteration of the properties of the packaging material would affect the shelf-life of the food product to be stored. The purpose of the investigation was to evaluate the suitability of two polypropylene-based materials with oxygen barrier, as an alternative to metal or glass, for canned oily products.

To this aim, the oxidative stability of an olive oil sample contained in the two different packaging materials was tested before and after autoclaving. Results were compared with those obtained on the same oil stored in glass.

The oxidative stability of the oil samples was investigated by accelerating the oxidation process using a reactor based on the use of high temperatures and over-pressure of oxygen.

Between the two polypropylene-based materials, the one showing higher stability after autoclaving was then subjected to an accelerated ageing process using a climate chamber in order to evaluate the effects of a shelf-life greater than six months at room temperature.

The results obtained confirm that the oxidation reactor is particularly useful for determining the packaging material that maintains the product in the freshest condition.

20. **Investigation of the Higher Oxidation Rates of Conjugated Fatty Acids Relative to Their Unconjugated Isomers.** P.G. Boakye[1], H.K. Abaidoo-Ayin[1], G.D. Strahan[2], W.M. Indrasena[3], V.T. Wyatt[2], S.A. Besong[1], and S.E. Lumor[1], [1]Delaware State University, USA, [2]USDA, ARS, ERRC, USA, [3]DSM Nutritional Products Canada Inc., Canada.

Generally, the rate of lipid oxidation is directly correlated to the degree of unsaturation. However, this has been found not to be necessarily true when conjugated fatty acids (CFAs) are considered. A recent study has reported that the oxidation rate of conjugated linoleic acid was significantly higher than those of linolenic and arachidonic acids, but comparable to that of docosahexaenoic acid. This observation deserves further investigation in order to elucidate the underlying mechanism. Our hypothesis is that the observed disparity in the rate of oxidation might be due to the different rates at which vinylic and divinylic protons are abstracted from the conjugated and unconjugated fatty acids, leading to the formation of 1-3 butadiene and 1-4 pentadiene radicals, respectively. Therefore, the goals of this investigation are to confirm and test our hypothesis regarding the higher rates of CFA oxidation. In this investigation, the oxidation rates of conjugated linoleic acids will be compared to those of their unconjugated isomers and other polyunsaturated fatty acids. Oxidation induction time will be determined using DSC, and the rates of free-radical abstraction of vinylic and divinylic protons by ^{1}H NMR. Furthermore, the formation rates of pentadienyl and butadienyl radicals will be assessed by ESR.

21. **Essential Oil of *Pituranthos scoparius* Delays Crystallization of Palm Oil.** A. Chikhoune[1], A. Boudjellal[1], and S. Martini[2], [1]Equipe Maquav, Laboratoire BIOQUAL, INATAA, Universite´ Fre`res Mentouri Constantine, Algeria, [2]Dept. of Nutrition, Dietetics, & Food Sciences, Utah State University, USA.

The attempt of this study is to study the influence of adding the essential on the crystallization behavior of palm oil at 20, 21, 22, 23, and 24°C. The essential oil was recovered by hydrodistillation from an Algerian plant named locally "Guezzah". It was applied at a concentration of 5% (w/w). Differential scanning calorimetry (DSC) was used to evaluate the isothermal crystallization of the samples and their melting behavior; and polarized light microscopy (PLM) was used to evaluate crystal microstructures. The melting profiles along with the isothermal profiles of the palm oil containing the essential oil depicted differences in shapes but also in enthalpies. In addition, a delay of crystallization was observed in the isothermal part. The PLM revealed different shapes and sizes of the crystals for the palm oil containing the essential oil compared to those of palm oil without essential oil. Based on the evidence obtained by DSC and PLM, it is suggested that the presence of the essential oil in palm oil leads to a delay of its crystallization. Therefore, the essential oil of *Pituranthos scoparius* can be used industrially to give some melting properties and sensorial quality for some fat-based products.