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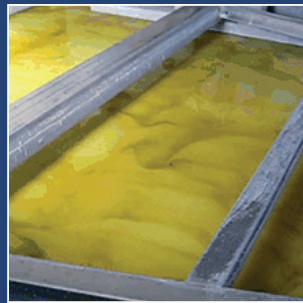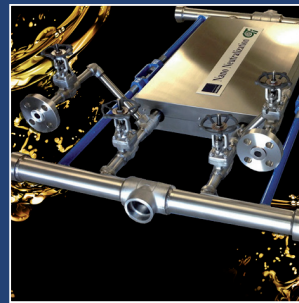
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Good vibrations: online and at-line monitoring of edible oils with vibrational spectroscopy

Laura Cassiday

In almost every industry, there is a drive toward smaller, smarter, more user-friendly instrumentation, and the edible oil industry is no exception. Moreover, edible oil producers want instruments that are less costly, more environmentally friendly, and capable of monitoring every step in the production process from oilseed or fruit to the finished product. Further down the supply chain, food manufacturers want to ensure that the edible oils they use meet specifications and are not rancid or adulterated. To help satisfy these demands, many researchers and companies have developed technologies based on vibrational spectroscopy that can continuously monitor edible oil parameters on the production line (online), as well as portable devices that enable workers to obtain a quick snapshot of oil characteristics at different points during production (at-line).

- **Vibrational spectroscopy encompasses mid-infrared, near-infrared, and Raman spectroscopy.**

- **Online and at-line (portable) infrared spectrometers allow rapid, reliable monitoring of edible oils at all stages of production.**

- **In addition, infrared spectroscopy can be used to assess the quality and authenticity of edible oils and products that contain them.**

VIBRATIONAL VARIETIES

There are three major types of vibrational spectroscopy: mid-infrared (MIR), near-infrared (NIR), and Raman spectroscopy. All measure the effect of electromagnetic radiation on vibrational states of molecules in a sample. IR spectroscopy uses light within the MIR (2.5–25 μm wavelengths) or NIR (0.7–2.5 μm) region to excite vibrations in molecules. The IR interacts with the molecules and causes their chemical bonds to vibrate. "Each functional group in a molecule, depending on the nature of the functional group and also on the molecules that surround it, is going to have different vibrations at different frequencies," explains Luis Rodriguez-Saona, professor of food science and technology at Ohio State University, in Columbus, USA. "We are able to identify different compounds based on these unique vibrations."

In contrast, Raman spectroscopy irradiates molecules in a sample with a laser of fixed wavelength, which causes molecules to vibrate and scatter the laser light. "Depending on the type of functional groups present in a sample, light is going to be scattered at different frequencies," says Rodriguez-Saona. Because Raman is a confocal technique, any out-of-focus signal is eliminated. As a result, Raman can analyze samples through transparent packaging such as glass or plastic bottles or bags, eliminating the need to remove the sample from its container (Ellis, D. I., *et al.*, http://doi.org/10.1039/c5ay02048d, 2015).

els through a sample placed in a spectrometer. The requirement for a very short path length creates problems for viscous samples such as oils, which must be placed in tiny capillaries for analysis. The path length limitation of MIR can be partially overcome by the use of a technique called attenuated total reflectance (ATR). In ATR, the IR light is passed through a crystal that is in contact with the sample. The IR penetrates into the sample at a depth of only 3 µm or less, compared with 10–50 µm for conventional transmission MIR spectroscopy (Cozzolino, D., http://doi.org/10.1039/c5ay01792k, 2015). However, this method requires the oil to be placed on an ATR crystal for measurement, which, again, could hamper automated online analysis. Mettler Toledo (Griefensee, Switzerland) offers an online FTIR ATR system called the ReactIR 45P.

"Raman is a technology that is attracting more attention, especially in the food industry," says Rodriguez-Saona. Although online Raman systems are more unusual, Kaiser Optical Systems (Ann Arbor, Michigan, USA) sells four versions of Raman analyzers for online process control, such as the RamanRxn4 analyzer. In the past, a limitation of Raman has been that the laser commonly used for the technique (a red laser, with wavelength of 750 nm) tends to excite fluorescence as well as scattering. "New systems are actually using a near-infrared laser, which is at 1064 or 1030 nm, that reduces the effect of fluorescence," says Rodriguez-Saona. "Now, it also diminishes the signal, so here's where the technology has advanced in getting detectors that are going to be able to detect very low levels of scattered photons. So we're seeing more of the Raman with near-infrared lasers, which is something that is very exciting."

INSIDE AN IR SPECTRUM

Of the three types of vibrational spectra, the MIR spectrum is the most straightforward to relate to specific functional groups in a molecule (Fig. 1). For an edible oil, the higher-frequency end of the spectrum (3,700–3,400 cm^{-1}) corresponds to hydroxyl

Raman spectroscopy can also be combined with microscopy to identify and quantify chemical distribution within a sample.

Each technique has its own advantages and limitations. Typically, MIR spectra are easier to interpret because the MIR excites only fundamental stretching and bending vibrations of C-H, C-O, O-H, and N-H bonds, and the signals are usually more intense and distinct than those in NIR spectra. Higher-energy NIR can excite complex vibrations, known as overtones (doubly excited vibrational modes) and combinations (two or more vibrational modes occurring simultaneously). In NIR spectra, the overtone and combination bands can overlap, making interpretation more difficult. However, the combination bands in NIR spectra can provide more complex structural information than can be obtained from MIR spectra (Cozzolino, D., http://doi.org/10.1039/c5ay01792k, 2015). In addition, NIR can analyze samples through plastic bags.

NIR is more amenable to online analysis because conventional MIR is limited to very short path lengths of only a few micrometers. Path length refers to the distance light trav-
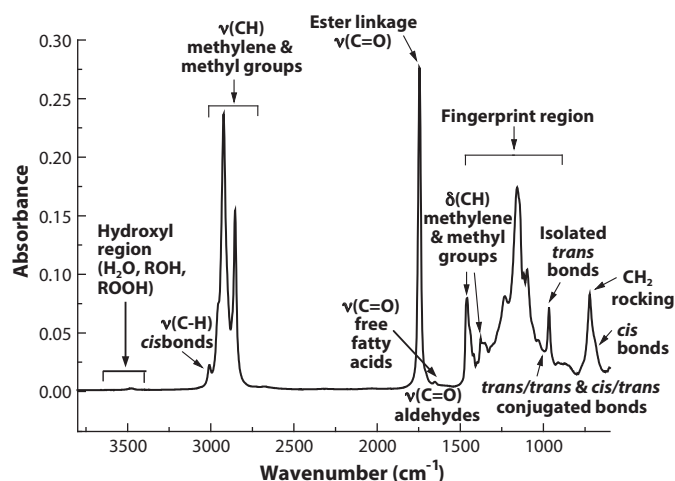

FIG. 1. The mid-IR spectrum of an edible oil collected on an attenuated total reflectance (ATR) crystal. Labels indicate absorption bands or regions associated with triglycerides or other constituents that may be present in an oil. FFA, free fatty acids. *Inform* 11: 614–620.

groups (e.g., water and hydroperoxides). If an edible oil sample is clean, dry, and mostly unoxidized, there is no appreciable MIR absorption in this region (van de Voort, F. R., and Sedman, J., *Inform 11*: 614–620, 2000). At lower frequencies (3,025–1,500 cm^{-1}), different functional groups such as methylene, methyl, aldehyde, and ester groups absorb MIR at specific frequencies. At ~1,750 cm^{-1}, a strong band arises from the ester linkage attaching fatty acids to the glycerol backbone of triglycerides. On the right shoulder of this band, a small band corresponding to the carboxyl group of free fatty acids can be observed, if lipolysis has occurred in the sample. In the same region, small carbonyl absorption bands of aldehydes and ketones are seen, if the oil is oxidized.

A region between 1,500 and 900 cm^{-1}, called the "fingerprint region," has a pattern of bands that is highly characteristic of molecular composition, and can therefore be used to identify substances. The fingerprint region contains structural information such as whether trans-containing triglycerides are present in the oil. If more than one double bond is present in a particular triglyceride, the fingerprint region can also indicate whether the double bonds are in trans/trans or cis/trans configurations.

Thus, an abundance of qualitative data, such as edible oil composition, moisture content, and oxidative status, can be gleaned from an MIR spectrum. In addition, quantitative data on oil composition can be obtained. According to the Beer-Lambert Law, the concentration of a molecule or functional group is proportional to its absorbance, or peak height. Therefore, vibrational spectroscopy can provide both qualitative and quantitative information about the components in an edible oil sample.

AN EVOLVING TECHNOLOGY

IR spectroscopy has been used in the food industry for decades, with much of the fundamental work being carried out between 1945 and 1965 (van de Voort, F. R., *et al.*, http://doi.org/10.1007/s12161-008-9031-6, 2008). In the early days, IR spectroscopy was used almost exclusively for qualitative purposes, mainly molecular characterization. An exception was the widespread use of MIR during the 1950s to determine trans isomers in edible oils and fats. Then, interest in IR spectroscopy lagged as newer techniques, such as gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy, became available.

In the 1970s, the advent of Fourier Transform (FT) IR spectroscopy sparked renewed interest in quantitative IR analysis. These instruments were a substantial improvement over the so-called dispersive IR instruments introduced in the 1940s. The old instruments scanned sequentially through wavenumbers of light. In contrast, FTIR instruments collect data from all wavenumbers simultaneously, and then translate the resulting interference pattern into an IR spectrum. FTIR instruments are faster, more sensitive, and more accurate than the older instruments. They have fewer moving parts prone to slippage, and allow no stray light. The digital processing capabilities of FTIR instruments enabled new chemometric techniques for

FIG.2. The Agilent 4500 portable FT-MIR instrument is rugged, compact, and easy to use, making it ideal for at-line measurements.
Credit: Agilent

qualitative and quantitative analysis. In the late 1980s, more compact, robust, and inexpensive FTIR instruments became available, which furthered the popularity of the technique (van de Voort, F. R., *et al.*, http://doi.org/10.1007/s12161-008-9031-6, 2008).

Nowadays, "there is a trend toward usability and portability," says Frederic Prulliere, business development manager at Agilent, in St. Louis, Missouri, USA. "People want instruments that are smaller, smarter, easier to use, and that can give you an answer right away. Space is often at a premium. With portable devices, you can bring the instrument where it is needed." Agilent offers several portable and handheld FT-MIR instruments, such as the 4500 Series Portable FTIR (Fig. 2.). Prulliere notes that Agilent's portable FTIR systems are very user-friendly. "You don't need to have sophisticated, highly trained personnel, as you do with other techniques such as GC-MS." Currently, Agilent does not offer FTIR instruments for online analysis. "Cost is a consideration," says Prulliere. "An online system might cost $80,000 to $100,000, while a portable (at-line) system is only about $28,000."

Online instruments on the market are typically based on FT-NIR. Bruker Optics (Billerica, Massachusetts, USA) offers the MATRIX-F FT-NIR spectrometer (Fig. 3), which can simultaneously measure multiple parameters of an oil at various stages of production or use. The instrument can be housed in a cabinet, away from hostile conditions on the factory

floor, with fiber optic probes reaching difficult-to-access samples in tanks, bypasses, or conveyer belts. Up to six sensors can be multiplexed in a single MATRIX-F spectrometer. Other manufacturers such as Foss (Hillerød, Denmark), Unity Scientific (Brookfield, Connecticut, USA), and Thermo Scientific (Waltham, Massachusetts, USA) also offer at-line and online FT-NIR solutions.

QUALITY CONTROL

At-line and online FT-NIR systems are finding applications in quality control and process monitoring during each step of edible oil production, from checking the incoming oilseeds to quality testing of the finished product (Bruker, http://tinyurl.com/BrukerFTNIR, 2015). FT-NIR spectrometers can non-destructively analyze both liquid and solid samples. When oilseeds arrive at a processing plant, FT-NIR can be used to check parameters like oil and moisture content, amount of free fatty acids, and fatty acid composition. The high-oleic status of specially bred oilseeds (e.g., high-oleic sunflower seeds) can be verified. Workers simply place ground or unground oilseeds in a cup with a glass bottom, and the FT-NIR spectrometer completes multiple analyses in less than one minute. In contrast, sending seeds to outside labs for analysis can take days and hold up production.

During oilseed storage, moisture analysis by FT-NIR can help monitor conditions and drying processes to discourage the growth of bacteria, fungi, and mold. To evaluate oil extraction efficiency, FT-NIR can monitor moisture and oil levels in seeds, expeller cakes, and extracts. The extracted crude oil can be analyzed for free fatty acids, phospholipids, and waxes in order to optimize refining conditions. And each step of the refining process can be monitored by online FT-NIR for real-time process measurements.

Furthermore, FT-NIR can be used to assess fat modification processes such as fractionation, interesterification, and hydrogenation. The technique can evaluate the physical and chemical properties of the finished oil, including fatty acid profile, free fatty acid content, the presence of *trans* fats, iodine value (IV, a measure of the amount of unsaturation), and solid fat content. And finally, FT-NIR can analyze oil byproducts (which can be used as raw materials for animal feed and other products) for oil, protein, moisture, fiber, and ash content.

Before FT-NIR and FT-MIR instruments became widely available, companies typically had to send samples to off-site labs, where edible oils were analyzed for quality parameters by wet-chemistry (e.g., titrations or chemical reactions) or chromatographic techniques. "A lot of it was based on just wet chemistry," says Chris Dayton, director of fats and oils processing at Bunge Limited in White Plains, New York, USA. "And then we would have holdups in the system to qualify a tank of oil or protein before it was shipped. So it made for larger inventories and a higher risk of being out of specification." Bunge, a global agribusiness and food company that manufactures edible oils and margarines, among many other products, uses both at-line and online IR systems for process monitoring, says Dayton. "You know instantaneously what's going on so you can use statistical process control to run your operation," he says. "You're able to meet customer specifications with the least amount of cost involved."

Traditional methods of analysis are usually designed to measure only one parameter, whereas FT-MIR and FT-NIR can analyze multiple parameters simultaneously. In addition, the IR methods are safer and more environmentally friendly than wet-chemistry or chromatographic methods because no hazardous chemicals or solvents are involved. In most cases, no sample preparation is required—the oilseed or oil is placed (either

FIG. 3. The Bruker MATRIX-F FT-NIR online system can remotely access hard-to-reach samples through fiber optics technology.
Credit: Bruker

Information

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manually or automatically) directly into the instrument for analysis. Therefore, no special skills are needed, and there is little or no chance of operator error. Automated chemometrics (multivariate statistical analysis) packages in commercial systems can translate IR spectra into easy-to-understand qualitative or quantitative data. In the simplest terms, chemometric analysis involves comparing test IR spectra with stored spectra of known reference materials. For quantitative analyses, chemometric models can be developed that correlate FT-MIR and FT-NIR spectra with results from standard methods of analysis or with reference standards containing known amounts of analytes.

EXAMPLES OF APPLICATIONS
Frying oils
In commercial frying operations, fats and oils are used continuously at high temperatures. During frying, hundreds of chemical reactions occur that change the physical and sensory properties of the oil and of the fried food. Oxidation of frying oils can cause off-flavors, foaming, and the formation of unhealthful compounds such as aldehydes and monomeric oxidized triglycerides (MonoxTG). Several wet-chemical and chromatographic methods have been developed to monitor oxidation products in frying oils. For example, AOCS Official Method Cd 18-90 uses a chemical reaction to determine anisidine value (AnV), a measure of aldehyde production. AOCS Method Cd 20-91 uses column chromatography to analyze total polar compounds (TPC) in frying fats. Although these methods are well validated, they are relatively slow, require a well-equipped lab and skilled staff, and necessitate the use (and subsequent disposal) of solvents and toxic chemicals.

To establish FT-NIR as a tool for monitoring frying oil quality, researchers recently conducted a large study of 400 fresh and used frying oils collected from restaurants, bakeries, industrial frying plants, fisheries, and other frying industries in Germany (Gertz, C. and Behmer, D., http://doi.org/10.1002/ejlt.201300270, 2014). The oils were of varied types and degrees of unsaturation, and were used to fry a variety of foods such as potato chips, battered fish, donuts, and chicken. The researchers used FT-NIR to simultaneously measure parameters such as AnV, TPC, MonoxTG, di- and polymerized triacylglycerols (DPTG), acid value (AV, a measure of free fatty acids), and fatty acid composition, including *trans* fats. They then analyzed the same samples using standard methods of the German Society of Fat Science (DGF), which were based on wet chemistry and chromatography. By comparing the FT-NIR spectra to the known values determined by standard methods, the researchers used a partial-least-squares (PLS) algorithm to construct calibration models. Then, they tested the models on a validation set of oils. The researchers found that all of the FT-NIR measurements correlated well with those determined by official standard methods. In the future, fast food restaurants or other frying operations could use online or at-line FT-NIR systems to decide when it is time to discard used frying oils.

In 2013, the German Society for Fat Science issued a standard method [DGF C VI 21a (13)] for using FT-NIR to determine DPTG, IV, AV, and AnV in used frying fats and oils (Gertz, C., *et al.*, http://doi.org/10.1002/ejlt.201300221.)

Potato chip oils

Lipids comprise 35–44% of potato chips (Aykas, D. P. and Rodriguez-Saona, L. E., http://doi.org/10.1039/c5ay02387d, 2016). The most common frying oils for potato chips are corn, canola, sunflower (mid- and high-oleic), high-oleic safflower, and cottonseed. For economic purposes and to extend shelf life, many potato chip manufacturers use blends of oils, rather than a single vegetable oil. Edible oils are one of the most counterfeited foods, and they may be adulterated with cheaper oils such as canola, soybean, and palm. Potato chip manufacturers may unknowingly receive shipments of adulterated vegetable oils, which then end up in the potato chips.

To develop at-line methods for potato chip oil authentication, Rodriguez-Saona and his coworker used a portable FT-MIR spectrometer equipped with an ATR crystal (Cary 360, Agilent Technologies Inc., Santa Clara, California, USA) to analyze 95 commercial potato chips (http://doi.org/10.1039/c5ay02387d, 2016). The researchers expelled the oil from the chips with a hydraulic press. Then, they measured various oil quality parameters using both FT-MIR and standard techniques: for the fatty acid profile, gas chromatography-fatty acid methyl ester (GC-FAME) analysis; for peroxide value (PV), AOCS Official Method Cd 8-53; for free fatty acids, AOCS Method Ca 5a-40; and for AnV, AOCS Method Cd 18-90.

Using chemometrics [PLS and soft independent modeling of class analogy algorithm (SIMCA)], the researchers correlated the MIR spectra with the reference values obtained by the standard methods. They then tested the calibration model on 13 additional potato chip samples. The fatty acid profiles determined by portable FT-MIR correlated well with those obtained by GC-FAME. Eight of the potato chip samples contained only one type of oil, whereas five had mixtures. Three samples had
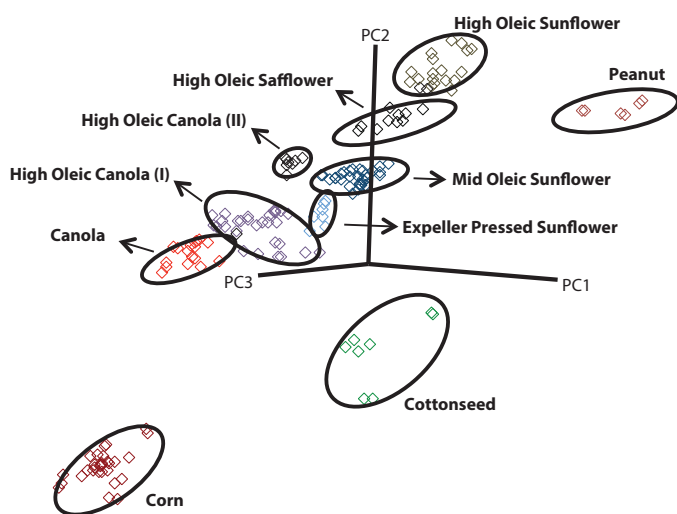
FIG. 4. (a) SIMCA 3D projection plots of second derivative-transformed spectral data collected by a portable FT-MIR spectrometer for frying oils extracted from commercial potato chips. Different oil types form distinct clusters. **(b)** SIMCA discriminating plot based on the MIR spectra of oils using a portable FT-MIR spectrometer, showing bands and regions responsible for class separation. Courtesy of Luis Rodriguez-Saona

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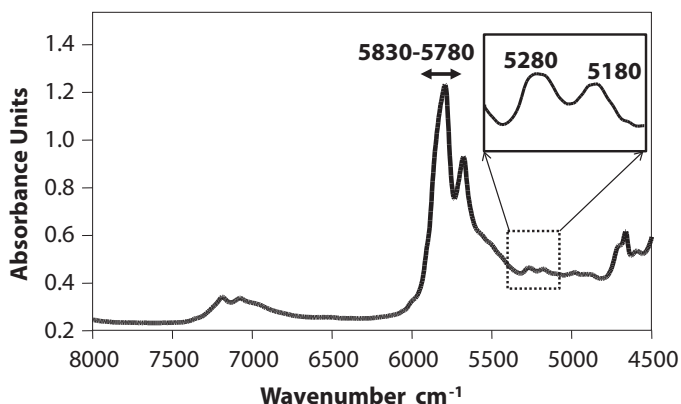
FIG. 5. FT-NIR absorption spectrum of an extra virgin olive oil, showing the presence of weak yet highly characteristic bands at 5180 and 5280 cm⁻¹. Credit: *Lipids*

mislabeled oils sources: The potato chip labels claimed only sunflower oils, but they also included cottonseed oil and at least one other oil. Using SIMCA, the researchers showed that different oil types formed distinct clusters (Fig. 4 , page 11), providing a rapid screening tool for potato chip manufacturers.

In other work, Rodriguez-Saona and colleagues used a portable FT-MIR spectrometer and similar chemometric approaches to characterize the fatty acid compositions of dietary omega-3 oil supplements (Plans, M., *et al.*, http://doi.org/10.1007/s11746-015-2666-8, 2015) and to differentiate conventional and organic bovine butters (Plans Pujolras, M., *et al.*, http://doi.org/10.1007/s11746-015-2591-x, 2015).

Olive oil authentication

As a high-value oil, extra virgin olive oil (EVOO) is commonly adulterated with cheaper seed oils such as sunflower or hazelnut. Currently, no method is available to rapidly authenticate EVOO and identify and quantify adulterants (Azizian, H., *et al.*, http://doi.org/10.1007/s11745-015-4038-4, 2015). Therefore, Hormoz Azizian, Magdi M. Mossoba, and colleagues used the MATRIX-F and –MPA FT-NIR spectrometers (Bruker Optics) to analyze EVOO, as well as EVOO spiked with known amounts of vegetable oil adulterants.

The researchers noticed that the FT-NIR spectrum of pure EVOO contains two characteristic minor bands near 5280 and 5180 cm⁻¹, which were attributed to volatile and non-volatile components, respectively (Fig. 5). When the researchers spiked the EVOO with fully refined olive oil, palm oil, or other vegetable oils, the band near 5280 cm⁻¹ team decreased in intensity. The researchers used these two bands and other spectral regions to develop PLS calibration models. Because the vegetable oil adulterants had different fatty acid profiles, the team had to develop four separate PLS models. When they analyzed a commercial sample with suspected adulteration, the researchers fit the FT-NIR data to one of the models, which predicted 11.7% adulteration with a high-linoleic-acid oil. The researchers confirmed this result by spiking a test sample with known amounts of soybean oil, which is high in linoleic acid.

FUTURE PROSPECTS

Although vibrational spectroscopy has been available for decades, many food companies have yet to embrace the technology, partly due to familiarity with the old methods, and partly because of misconceptions that vibrational spectroscopy is too complex or expensive. "Based on my own experience, even when the benefits of a technology are as clear-cut as in the case of FTIR spectroscopy, overcoming the inertia of familiar standardized procedures can still be a daunting task, especially in the cost-conscious food industry," says Frederik van de Voort, emeritus professor and co-director of the McGill IR Group at McGill University in Montreal, Canada.

However, recent advances in optics and chemometrics, as well as the availability of online and at-line FT-MIR and FT-NIR spectrometers, argue that the technology merits a second look. "It's a very exciting time for this technology," says Rodriguez-Saona. "It seems that the technology is more amenable now to what the industry needs." In the not-too-distant future, portable vibrational spectrometers might even be placed in the hands of consumers, who could do their own quality checks of edible oils and foods at home or in supermarkets.

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Predicting the **interfacial tension change** at optimum formulation for **enhanced oil recovery**

Jean-Louis Salager, Ana Forgiarini, and Johnny Bullón

- It has been clear since chemical enhanced oil recovery (CEOR) research began in 1974, that the most important issue in surfactant enhanced oil recovery (EOR) is the attainment of an ultralow interfacial tension between the oil and water fluids in the reservoir conditions.

- Surfactant–oil–water systems were found to exhibit a low interfacial tension when the surfactant adsorbed at interface has exactly the same interactions with oil and water. This happens at the so-called optimum formulation, which corresponds to the minimum tension over a scan, the point at which a continuous change of a variable (like water salinity, oil and surfactant type, temperature) can alter the interactions between the adsorbed surfactant and the oil and water molecules.

- The present article is a simplified version of a previously published report that addressed, for the first time, the quantification of the minimum tension versus formulation variables. The report received the 2014 American Cleaning Institute's Distinguished Paper award at the 2015 AOCS Annual Meeting & Industry Showcases, May 3–6, in Orlando, Florida. With a companion review paper on tension performance, the work reported here shows that it is now possible to predict the variation of minimum tension γ^* by appropriately changing two formulation variables.

The chemical enhanced oil recovery (CEOR) of light crude oil with surfactant and polymer is probably an interesting alternative for the next 20–30 years at about \$15–20/Bl, due to a lower production cost than heavy crudes and shale oils. CEOR studies started in 1974, because of the oil embargo. During the next five years, considerable oil price increases pro- vided a strong incentive for fundamental and applied investigations to be conducted both in universities and industrial research centers. It is worth remarking that financing by the US government was associated with a free divul- gement of the results, an unusual situation that rapidly advanced understanding of the phenomena.

When the oil price went down in the early 1980s, such research was considerably reduced, though not completely abandoned. It started to increase 20 years later, but this time with lot of confidentiality.

From the very first years [1] of research, it has been clear that the most important issue in surfactant EOR is the attainment of an ultralow interfacial tension, say 10^{-3} mN/m or less, between the oil and water fluids in the reservoir conditions.

INTERFACIAL TENSION MINIMUM IN A FORMULATION SCAN

Surfactant–oil–water systems were found to exhibit a low interfacial tension when the surfactant adsorbed at interface has exactly the same interactions with oil and water. This takes place at the so-called optimum formulation, which corresponds to the minimum tension over a scan, the point at which a continuous change of a variable (such as water salinity, oil and surfactant type, and temperature) is able to alter the interactions between the adsorbed surfactant and the oil and water molecules. Fig. 1 shows what happens to the interfacial tension when various formulation variables are changed.

The formulation scan concept was proposed by Winsor [2] in the 1950s through the so-called interaction ratio R = Ao/Aw, where the A's are the interactions of the surfactant with oil and water. At R = 1 a three-phase behavior is exhibited with a bicontinuous microemulsion at equilibrium with excess water and excess oil phases, and a very low tension between oil and water is attained [3]. However the A's cannot be well estimated in practice and the concept had to be rendered by more accurate numerical correlations for EOR. By the late 1970s, a simple relationship was empirically found between all basic formulation variables to attain the minimum tension when one of the variables was scanned.

For anionic surfactants [4], it was a linear relation as follows:

$$\ln S - K\, ACN + \sigma + f(A) - a_T\,(T-25) = 0 \qquad (1)$$

For polyethoxylated nonionic surfactants, a similar relation was found [5]:

$$b\, S - K\, ACN + \beta + f(A) + c_T\,(T-25) = 0 \qquad (2)$$

Where the variables are the physicochemical characteristics of the system. S is the salinity of the aqueous phase, ACN is the alkane carbon number of the oil phase or the equivalent EACN if it is not an n-alkane, σ and β are the characteristic parameters of the surfactant, f(A) and $\phi(A)$ are the contribution of the type and concentration of alcohol cosurfactant, and T is the temperature. K, a_T, and c_T are constant. The slight differences between the two equations are not conceptual, but are typical of the surfactant type. The salt effect on a nonionic surfactant is very weak, i.e., the b coefficient is small so
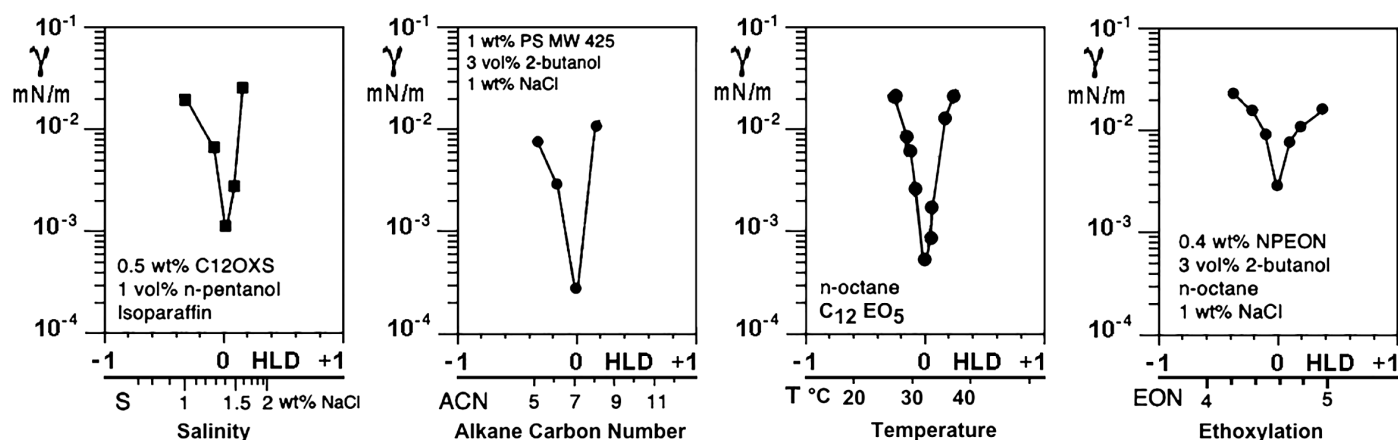

FIG. 1. Tension variation with different variables for anionic (left) and nonionic (right) surfactant systems: C12OXS: dodecyl orthoxylene sulfonate, PS Petroleum Surlfonate Witco 10-80, C12EO5: dodecyl alcohol pentaethoxylate, NPEON: nonylphenol ethoxylate

that the contribution is weak, and a linear (bS) term is accurate enough in practice. An ionic surfactant is much more sensitive to salt, and the lnS is a more accurate term in the correlation. Additionally, since an ionic surfactant is a salt itself, a zero salinity actually does not exist. On the other hand, it is worth remarking that the temperature terms have different signs because of opposing effects.

These correlations were found to represent the surfactant affinity difference (SAD), or the difference of standard chemical potential of the surfactant when it is in oil or water. [6]. This difference is actually the driving force for the surfactant molecule to move from one phase to the other. A dimensionless expression of the hydrophilic-lipophilic deviation HLD (SAD/RT) was later proposed for simplicity [7]:

For ionic surfactants $HLD = \ln S - K\ ACN + s + f(A) - aT\ (T-25)$ (3)

For nonionics $HLD = b\ S - K\ ACN + b + f(A) + cT\ (T-25)$ (4)

At HLD = 0, the situation is the same as when R = 1 and an optimum formulation in a scan is attained with a minimum tension and most of the time a three-phase behavior. More information on optimum formulation may be found in [1,8]. Fig. 1 indicates that when the formulation is calculated as HLD, the optimum formulation for minimum tension is at HLD = 0. However, it is seen in the different graphs that the value of the minimum tension is not the same, but depends considerably on the system. Consequently, when many unidimensional scans are carried out, some exhibit a lower tension minimum γ^*, which results in a better performance.

The actual low value of the interfacial tension minimum has been found to vary from case to case, and though some hints are available in the 200 references reported in a recent review [9], no general relationship has been available up to now, probably because too many variables are involved, often with very complex interactions. On the other hand, since two variables (at least) must be changed to pass from an optimum HLD = 0 equation to another, it is not always easy to know which variable is responsible for a good or bad change.

This explanation is a simplified version from a previously published report that dealt for the first time with the quantification of the minimum tension versus formulation variables [10]. The report received the 2014 American Cleaning Institute's Distinguished Paper award at the 2015 AOCS Annual Meeting & Industry Showcases, May 3–6, in Orlando, Florida. With a companion review paper on tension performance [9] the work reported here shows that it is now possible to start predicting the variation of minimum tension γ^* by appropriately changing two formulation variables.

The data used comes from a publication [11] exhibiting high-precision measurements of the tension at equilibrium in a very simple ideal system in which there are only four independent variables (the head and tail of an oligomerically pure nonionic surfactant, the n-alkane carbon number, and the temperature), with no possible mixture or partitioning troublesome known effects. From these data, the optimum formulation condition is found to be very accurately represented by the following linear relationship [10]:

$$HLD = SAD/RT = 2.00 + 0.34\ SACN$$
$$- EON - 0.15\ ACN + 0.05\ (T-25) = 0 \quad (5)$$

SACN is the surfactant alkyl carbon number (its hydrophobic tail length), EON is the number of ethylene oxide groups (its head group hydrophilicity), ACN is the n-alkane carbon number, and T is the temperature in °C. The term 2.00 is the integration constant [7] independent of the used variables.

PERFORMANCE EVALUATION

Sixty years ago Winsor proposed that the performance between two optimum cases be compared through a dual change in R ratio numerator and denominator, without changing the R unit value [2,12]. With the HLD concept, the comparison is essentially the same. The comparison could be carried out by changing (at least) two of the variables, while keeping the optimum formulation by maintaining the HLD = 0 condition.

For the present case with four variables, which will be called V1, V2, V3, and V4, the HLD = 0 condition may be written as:

$$HLD = a_0 + a_1\ V1 + a_2\ V2 + a_3\ V3 + a_4\ V4 = 0 \quad (6)$$

From this condition only three variables (V1/V2/V3) are actually independent so that:

$$a_1\ V1 + a_2\ V2 + a_3\ V3 = -a_0 - a_4\ V4 = constant \quad (7)$$

In a three dimensional space V1-V2-V3 this is the equation of the plane indicated in Fig. 2, where according to the example V1, V2, and V3 are EON, SACN, and T, respectively, while V4 is the oil ACN. This ACN is what makes it possible to place the plane. It is calculated by the intersection of the plane with the V1 axis, at V2 = 0 and V3 = 0. When V4 is changed, the plane is displaced parallel to itself.

In this optimum formulation plane, any constant V value is represented by a straight line. For instance, at fixed V3 (T = constant), then (horizontal) line equations are:

$$a_1\ V1 + a_2\ V2 = -a_0 - a_3\ V3 - a_4\ V4 = constant \quad (8)$$
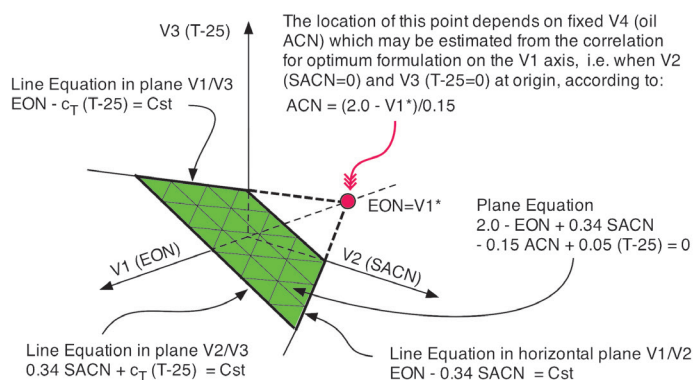
FIG. 2. Optimum formulation plane according to relation (7) [10]

If V1 and V2 are the two changed variables to make the comparison of the performance in two cases of optimum formulation, the dual change (DV1 and DV2) should be such that :

$a_1 \Delta V1 = - a_2 \Delta V2$ or the equivalent
differential relation $dV1/dV2 = - a_2/a_1$ (9)

These equations (8/9) represent the optimum formulation straight line in 2 dimensions reported in many experiments as the standard dual change with different couples of variables [4,5,12].

If the interfacial tension is plotted as a function of V1 and V2 (at constant V3 and V4), the surface aspect is like a valley as shown in Fig. 3, with the bottom of the valley being the minimum tension γ^* line. This line is projected as a straight line on the bottom plane according to equation [8]. If this minimum tension γ^* line is projected on the g-V1 (respectively γ-V2) vertical plane, the variation of the minimum tension γ^* is attained as a function of V1 (respectively V2).
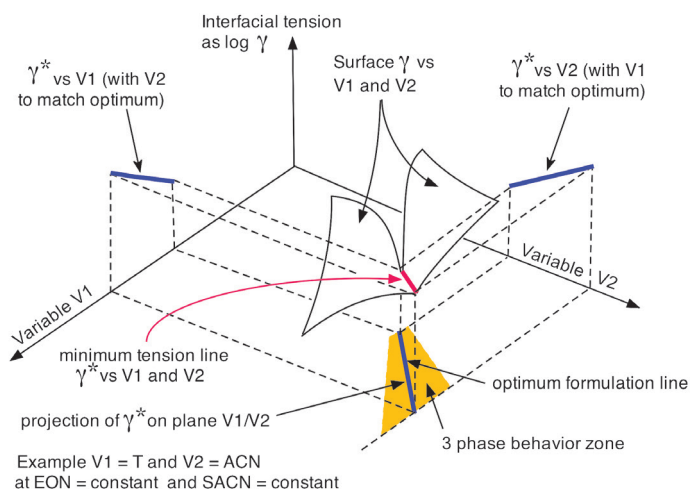
FIG. 3. Interfacial tension (as log γ) as a function of variables V1 and V2 at constant V3 and V4 [10]

The completely new result is that the minimum tension valley bottom line (log γ^* vs V1 and V2) is a straight line, because it projects as a straight line not only in the bottom V1/V2 horizontal plane, but also on the vertical planes, i.e. the log γ^*-V1 and log γ^*-V2 variations are straight lines. Fig. 4 indicates that this is the case whatever the selected V1/V2 variable pair. In Fig. 4 (top graph), V1 is the surfactant tail length SACN and the matching variable to attain optimum is temperature T, for fixed surfactant head group EON and oil ACN. It is clear that a dual increase in surfactant lipophilicity (SACN tail length) and in head hydrophilicity (by decreasing temperature) to maintain HLD = 0 produces a considerable increase in performance.

Note that in this graph the ordinate is the exponential of the value of the tension written as usual (its cologarithm). A tension of 10^{-2} mN/m is indicated as 2, 10^{-3} as 3, and so forth. The increasing cologarithm is downward, as is a lower minimum tension and performance increase.

Fig. 4 (bottom graph) contains various results. The black lines refer to various surfactant structures (fixed SACN and

EON) and it is clear that for the three cases, the lowest line, i.e. the better performance, is for the surfactant with both longer tail and longer head (SACN = 12/EON = 5) as forecasted in Winsor's premise 50 years ago. It is also clear that a higher ACN tends to decrease the performance as dashed lines (at constant ACN) tend to move upward. These are general trends but are not an exact comparison which implies a dual change. Other similar cases are shown in our previous article [10].
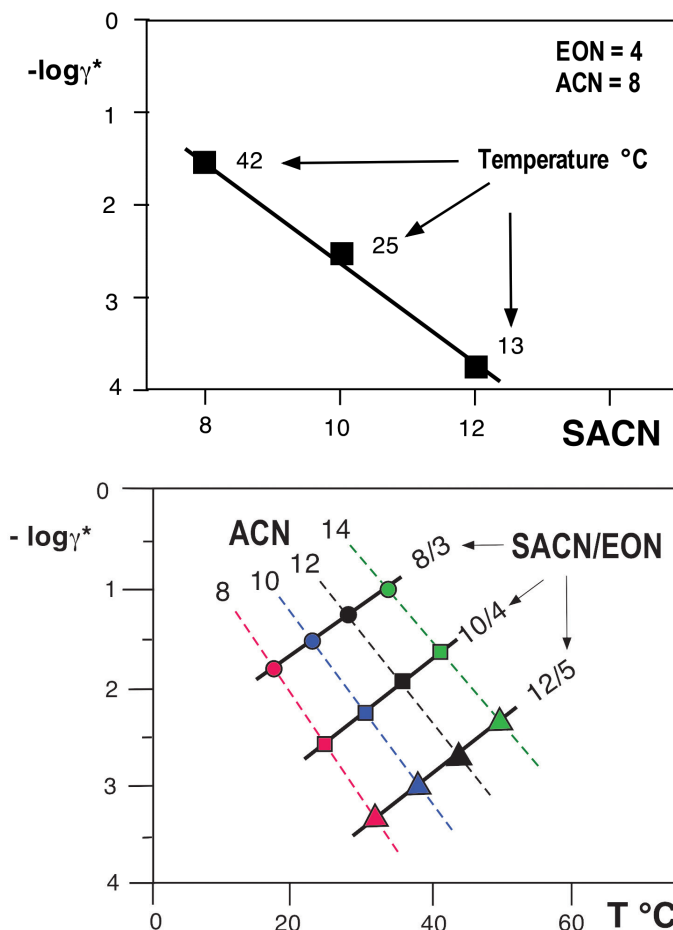
FIG. 4. Interfacial tension at optimum as -log γ^*, i.e., its cologaritm in $10^{-\gamma}$ mN/m, as a function of variable V1 (with matching V2 for HLD=0) at constant V3 and V4 [10]

Fig. 5 exhibits the same kind of results as Fig. 4 for given surfactants (SACN = V3 and EON = V4 fixed), and where the role of independent variables V1 and V2 is swaped. On the left graph, the variation of performance (-log γ^*) is shown as a function of ACN (V1) when the temperature (V2) is matched to attain optimum formulation. On the right graph, the performance is shown as a function of temperature (V1) when the ACN (V2) is changed (from 8 to 14) along the segments corresponding to the different surfactants. The slope of the segments indicate that both a decrease in ACN and a decrease in T tends to improve performance, and it is seen in the left plot where the surfactant with more important head and tail too is better, although ACN and temperature are also changed.

FIG. 5. Interfacial tension at optimum as -log γ* as a function of variable V1 (with matching V2 for HLD=0) for given surfactants (fixed V3=SACN and V4=EON) [10]

The question is: How much optimum tension variation is expected when a surfactant is changed? To answer this question, it is important to make a comparison of the performance of two surfactants (SACN/EON) at the same conditions of the other variables (ACN and T), in order to avoid their possible influence.

The way to do it is as follows using equation (6) of the optimum formulation condition in the 4-dimension space. If a formulation change is carried out from an optimum case to another, it should imply at least two (but up to four) variables differences indicated as Δ, so that:

$$a_1 \Delta V1 + a_2 \Delta V2 + a_3 \Delta V3 + a_4 \Delta V4 = 0 \tag{10}$$

Now, if the first change is a dual one (V1/V2), according to the correlation expression so that:

$$a_1 \Delta V1 + a_2 \Delta V2 = 0 \tag{11}$$

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the remaining eventual variations in V3 and V4 should satisfy

$$a_3 \Delta V3 + a_4 \Delta V4 = 0 \tag{12}$$

It is obvious that the simplest way to satisfy equation (12) is with no change at all for both variables, i.e., ΔV3 = 0 and ΔV4 = 0, so that the only change is according to equation (11). This is what happens in Fig. 5 (bottom plot) passing from surfactant SACN = 8/EON = 3 to surfactant SACN = 11/EON = 4 at constant ACN and T, i.e. a vertical change along the left arrow, which produces a reduction of γ* by a factor 30 (-logγ* increases 1.5 unit). This is identical to the change from surfactant 10/4 to 13/5 (right arrow) with the same dual variation 3 ΔEON = ΔSACN which exactly corresponds to equation (5) coefficients. It means that the dual variation is carried out along the optimum formulation straight line in the valley or in the bottom plane in Fig. 3.

Since the segments are parallel in Fig. 5 (bottom plot), this dual change is probably a general way to increase the performance by the same factor in the optimum interfacial tension. In other words, it may be considered as a prediction. By the way, this γ* reduction is found to be better compared with the change from surfactant 8/3 to surfactant 10/4 or 10/5, or any other in which equation (11) is not satisfied, so that a third change in T or/and ACN is also required. Of course a double change from 8/3 to 14/5 would be even better, but it also could result in a precipitation problem—a limit which is a classical problem in practice.

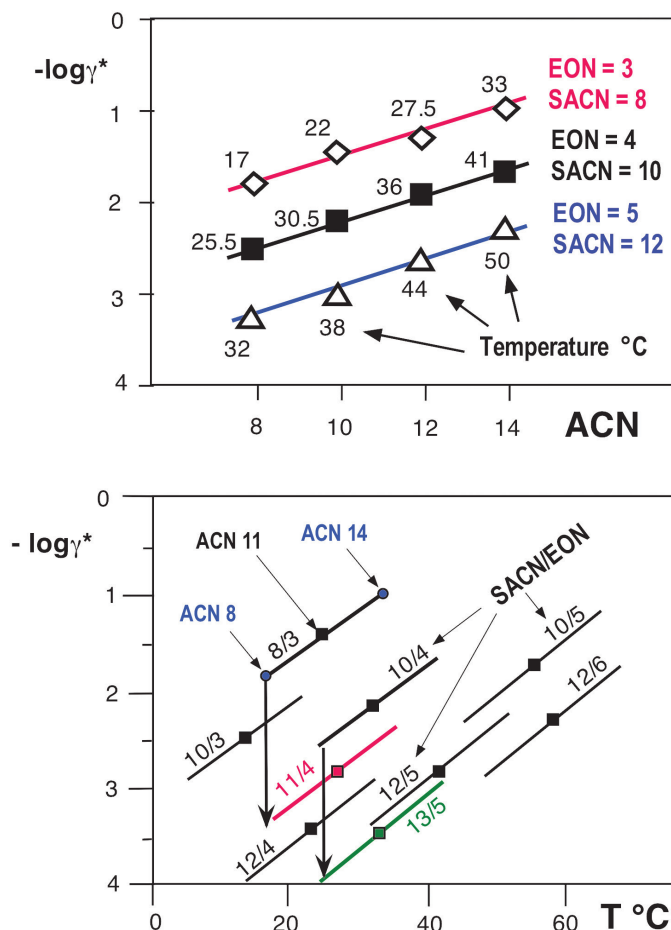As discussed in details elsewhere [10], the iso-performance contours (constant γ* lines) which may be plotted in

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the optimum formulation plane shown in Fig. 2, are essentially straight lines for this case. The best path to lower the minimum tension through formulation adjustments is perpendicular to the contours, along the largest γ^* tension gradient in the plane. Such a path is also a straight line that should be followed in practice to improve performance until a compatibility limit is attained.

When more complex systems are used in practice, for instance with a proper mixture of three selected surfactants to produce a strong synergy, nonlinear mixing rules are found for the surfactant characteristic parameters and iso-performance contours are not straight lines but curved or even closed ones often exhibiting an overall minimum, as recently reported [13].

The presently reported guidelines for a simple surfactant–oil–water ternary show that in a simple system with ultrapure products, the HLD linear relationship is very accurate, and that the performance improvement in the minimum tension value by changing the formulation may be predicted. It is probably only a first approximation for real systems with many formulation variables and synergy effects, but it can facilitate the formulator work in selecting the most feasible experimental essays to be carried out.

The three authors are professors at University de Los Andes, Mérida-Venezuela. Jean-Louis Salager founded Laboratory FIRP (Formulation, Interfaces, Rheology and Processes) in 1978 (see http://www.firp/ula.ve). He was Editor-in-Chief of AOCS' Journal of Surfactants and Detergents *from 2008 to 2014. Johnny Bullón and Ana Forgiarini are the current director and deputy director of Lab FIRP. Jean-Louis Salager can be contacted at salager@ula.ve.*

MALDI MS applications for rapid analysis of food lipids

Sara E. Shinn

There are numerous analytical approaches to extract and quantify lipids from intricate food matrices, as well as to characterize specific lipid properties and quality. Extracted lipids may be converted into more volatile fatty acid methyl esters (FAMEs) to determine total fatty acid composition by gas chromatography mass spectrometry (GC/MS). Alternatively, intact lipids can be separated by high performance liquid chromatography (HPLC) for subsequent detection and characterization.

- **Matrix-assisted laser desorption/ionization (MALDI) is an ionization method that produces intact lipid molecule species in a gaseous phase that can be subsequently separated and characterized by mass spectrometry (MS) alone or in tandem.**

- **Often MALDI MS analysis can be accomplished with little or no sample cleanup, and no chemical manipulation or derivatization is needed to obtain samples for MS analysis.**

- **This article examines selected MALDI MS applications for edible lipids analysis, and explores potential applications in food and lipid science.**

In the food oil industry, oils are described by the characteristics of total lipids, such as average molecular weight, lipid saponification, degree of unsaturation by iodine, and oxidation progression monitored by peroxide, anisidine, and thiobarbituric acid reactive substances (TBARS). Due to so many oil specifications, food lipid chemists are highly skilled in various instrumental and wet chemistry techniques. Usually a combination of approach is needed to fully characterize the lipids of interest. Furthermore, when lipids are converted to FAMEs for routine GC fatty acid analysis, any information about the original lipid structure is lost. Fortunately, matrix-assisted laser desorption/ionization (MALDI) is an ionization method that produces intact lipid molecule species (usually as cation-adducts) in a gaseous phase that can be subsequently separated and characterized by mass spectrometry (MS) alone or in tandem.

In the past few years, some of my collaborations have focused on determining useful MALDI MS methods for lipid analysis. In these we have attempted to develop and utilize rapid methods that employ simple sample preparation and minimal chromatography. Often MALDI MS analysis can be accomplished with little or no sample cleanup, and, unlike with FAMEs, no chemical manipulation (or derivatization) is needed to obtain samples for MS analysis. Although ion signal suppression is sometimes an issue, MALDI analysis is rapid, simple, and can be used for the initial analysis of crude extracts, followed by sample clean-up only as required. This article examines selected MALDI MS applications for edible lipids analysis, and explores potential applications in food and lipid science.

EXPERIMENTAL APPROACHES

MALDI methods published from our research group at The University of Arkansas for edible lipid analysis are generally robust [1–4]. It is useful to note that modifying both the lipid extraction and mass spectral procedures to make use of available organic solvents and instrument parameters have shown to provide similar, reproducible results. The MALDI matrix usually employed was 1M 2, 5-dihydroxybenzoic acid (DHB) in 90% MeOH, 10% aqueous 0.1% trifluoroacetic acid. For food oils, the

samples were directly combined with DHB matrix in a ratio of 1:100. For lipid-rich foods, either the Folch method or a rapid hexane/isopropanol extraction was used before MS analysis [1]. Mass spectra were obtained using a Bruker Ultraflex II MALDI time-of-flight (TOF) MS with typical operating conditions. The operating parameters were 200 Hz laser pulses in the positive ion, and reflectron modes. The extraction voltage was nominally 25 kV, and matrix suppression was set to m/z < 200. Parameters were adjusted to optimize sensitivity and resolution for ions between 400–2000. Data were acquired and processed using FlexControl 3.0, FlexImaging 2.0, and Compass 1.2 software (Bruker, Billerica, Massachusetts).

FOOD OILS

Food oil analysis can have many objectives: to differentiate and quantify the lipids present, to determine fatty acid composition, to determine oxidative status, or even possibly to detect economic adulteration. Oil fatty acid analysis by FAMEs GC/MS is done by most labs to define fatty acid composition. This method requires extraction, chemical derivation, and a chromatographic step. In contrast, MALDI MS allows direct analysis of intact triacylglycerol (TAG), without derivatization or separation [2]. One issue that may arise occurs when a sample contains polar lipids, which can suppress the ionization of the non-polar TAG. However, this direct method of analysis is quite reliable, as the TAGs in edible oils are almost entirely non-polar. MALDI MS can be used to identify food oils based on the characteristic ratios of TAGs. A food oil is simply combined with the DHB matrix on the MALDI target.

From the mass spectra, one can easily distinguish different oil types by their TAG-related ion abundance ratios. Fig. 1 compares the MALDI mass spectra of corn oil and lard, both of which have signature TAG profiles. Likewise other edible oils also have characteristic MALDI fingerprints.

Consequently, direct MALDI could provide a rapid tool for verifying the authenticity of expensive or imported food oils, determining an oil's average molecular weight and degree of unsaturation, or monitoring lipid oxidation and degradation. None of these research avenues has been extensively explored, and those attempting to explore them should be careful to minimize spontaneous fragmentation of

FIG. 1. MALDI mass spectra rapidly obtained from lard and corn oil. Shown are the sodium-adduct ions for the constituent triacylglycerol (TAG)
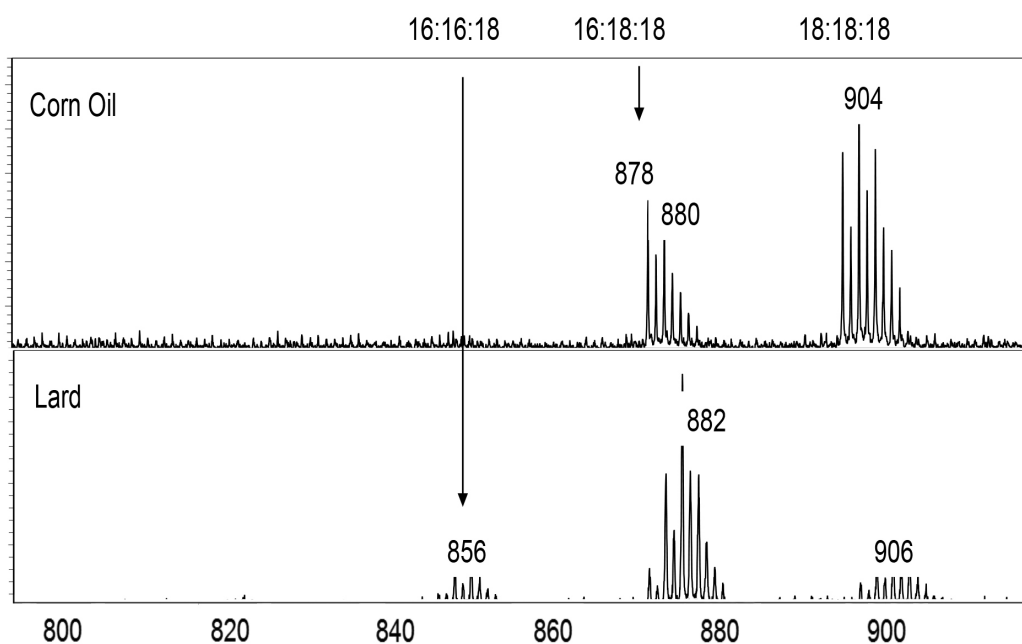
protonated TAG when using MALDI [3]. Although fragmentation does not preclude sodium adduct ion use for TAG identification, it does produce dia-cylglycerol (DAG)-like fragments at lower mass. However, such fragmentation will not readily occur in the MS if the matrix pH is adjusted so that MALDI produces only cation-adducts with alkali metals rather than protons [3].

LIPID-RICH FOODS

Recently, TAG and phospholipid (PL) composition in animal products has been well-described using chromatographic separation and MALDI MS analysis [3–6]. One group demonstrated that hydrogenating animal fat TAGs allowed detection of low-abundance short-chain lipids [5]. All species with the same fatty acids but different numbers of double bonds were converted into a single, common, fully saturated species of higher abundance. Bromination has been demonstrated to differentiate saturated and unsaturated TAG more clearly [5]. Fuchs *et al.* [6] coupled thin layer chromatography (TLC) with MALDI MS to analyze egg yolk PL after band separation, but the more abundant TAG surely present in the yolk samples were not reported.

Our group has focused on the rapid analysis of both TAG and PL in egg yolks, and more specifically, the real-time monitoring of deliberate changes in fatty acid composition, and the accompanying changes in the intact lipids during chicken feeding studies [4]. The yolk's fatty acid composition is easily modified by manipulation of the chicken's diet. These enrichments modify the ratios of saturated and unsaturated yolk fatty acids. It has been shown that egg enrichment can change the size, color, texture, organoleptic

Red: standard egg yolk
Green-CLA-rich egg yolk
Blue- omega-3 enriched egg yolk

FIG. 2. Egg yolk TAG region of MALDI mass spectra for standard commercial egg yolk, commercial omega-3 egg yolk, and CLA-rich egg yolks produced in our laboratory

properties, and hatchability of eggs, warranting the development of efficient and inexpensive surveillance methods for molecular changes. MALDI seemed like a useful and valuable approach.

However, egg yolk contains both polar and non-polar lipids, so suppression of the TAG signals needed to be addressed. Our response to TAG suppression was either to: 1. fraction-
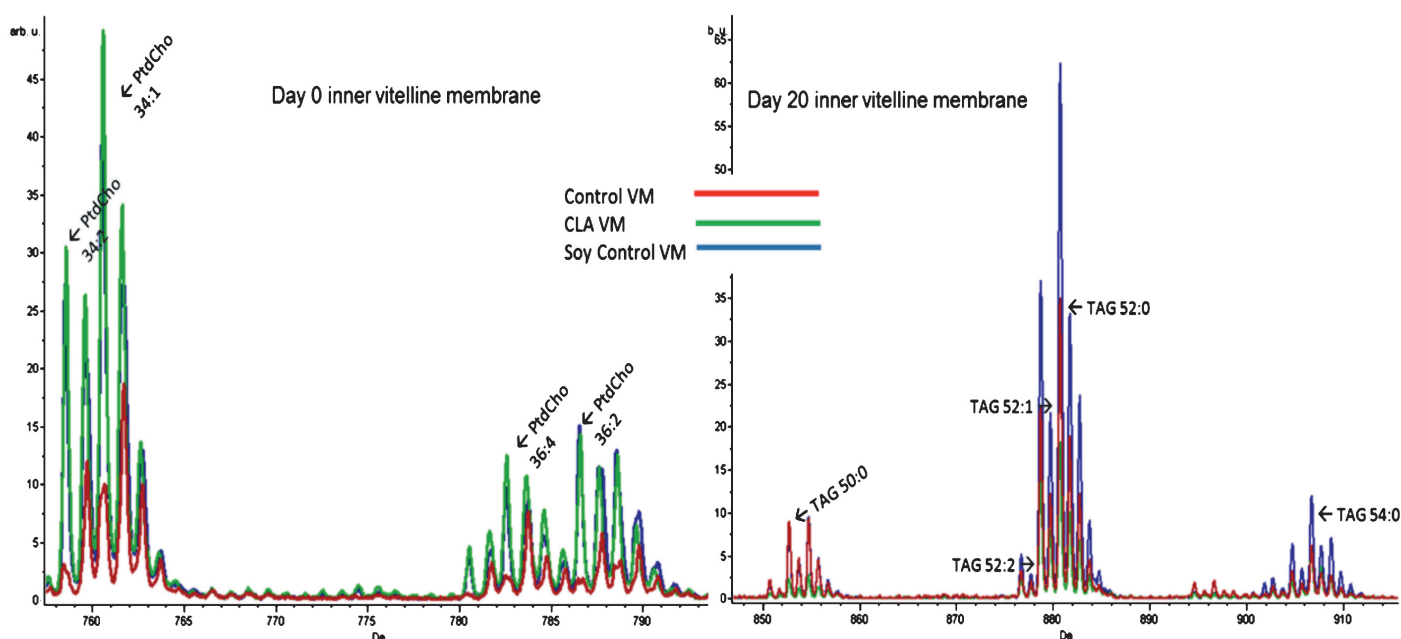
FIG. 3. Direct MALDI mass spectra of egg yolk vitelline membrane (VM) lipids resulting from dietary oil modification. In fresh eggs (day 0), distinguishable differences were seen among phosphatidyl choline (PtdCho) species, while TAG differences were prevalent from eggs refrigerated for 20 days.

ate polar and non-polar lipids with disposable PrepSep flo-risil extraction, or 2. apply TLC to separate lipid classes, and ionize directly off the TLC plate after matrix application [3, 4]. This means that recovery of the analyte from the TLC chromatographic medium is not required before MALDI analysis. Fig. 2 shows the mass spectra of the TAGs from a total lipids extraction of: standard control eggs, eggs enriched with conjugated linoleic acid (CLA), and commercially available omega-3 enriched eggs. The MALDI mass spectra show identifiable differences in certain lipid species abundancies, which cannot be detected by traditional FAME analysis.

In subsequent analyses of CLA-rich versus control egg yolks, the lipid profile of egg yolk vitelline membranes were determined using direct MALDI MS. This was interesting because vitelline membrane integrity does decrease during storage, but this deterioration occurs more slowly in eggs enriched with CLA. The lipid composition of this membrane had not been previously reported. The vitelline membranes of fresh eggs and those refrigerated for 20 days were isolated, mounted on a conductive glass slide, coated with DHB matrix, and lipids were directly ionized from the surface of the membrane. These samples were analyzed for differences in their lipid profiles and abundancies as a consequence of dietary lipid manipulation and storage. Fig. 3 shows mass spectra of lipid species that were significantly different among egg types. This analysis also determined differences in the lipid profiles of inner and outer membrane layers.

Understanding how dietary fat affects lipids in other animal tissues may be very beneficial in other animal nutrition and animal product enrichment research. MALDI MS is a rapid and repeatable analysis suitable for lipid-rich tissues, and it may also be useful in lipid metabolic studies. There is also opportunity to explore lipid biological and chemical induced oxidation by MALDI MS in lipid-rich food systems. MALDI provided the opportunity to rapidly, accurately, and fully characterize lipid species beyond their fatty acid content.

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Fractionation of insect oils: the case of yellow mealworm oil

Insects are a sustainable and efficient protein and lipid source, compared with conventional livestock. The sustainability of insects is based on efficient feed conversion rates and low production of greenhouse gases (Oonincx and De Boer, 2012). Moreover, insects need no drinking water and can grow on vegetable waste streams (Oonincx *et al.*, 2015). Insect oils and fats are used as ingredients in feed and have the potential to be used as food ingredients.

D.A. Tzompa-Sosa, J.M. Verbeek, and H.F.J. van Valenberg

- **Insect oils and fats are already used as ingredients in feed.**

- **Because such oils tend to be liquid even at low temperatures, their application in food may be limited.**

- **Could dry fractionation of insect oils make them more versatile for food applications?**

The oils from the insects studied in our laboratory are rich (>70%) in unsaturated fatty acids (FA) (Tzompa-Sosa *et al.*, 2014), which makes them liquid even at low temperatures (~5°C). This might restrict their use in the food industry—particularly for applications that require solid fat. Perhaps the application of insect oils in foods could be increased by changing the chemical composition and physical properties using dry fractionation (Wassell, 2014).

In the present work, we investigated dry fractionation of oil from yellow mealworm (*Tenebrio molitor*). The oil was obtained by Soxhlet extraction. Fractionation of the oil was studied using three cooling temperatures: 0, 2, and 4°C. Before fractionation, the oil was melted at 60°C for 30 min to eliminate the crystals in the fat, then the oil was placed in a water bath, filled with glycol, at the crystallization temperature (0, 2, or 4°C) for 24 h. The liquid fraction was separated from the solid fraction by centrifugation at 4,800 g for 20 min at the cooling temperature. Both fractions were placed in a separated tube and weighed. Then, we studied the colour and the thermal profile of both solid and liquid fractions. The FA composition of each fraction was analyzed by gas chromatography-flame ionization detector (GC-FID). The fractionation and analysis were done in duplicate.

YIELD AND COLOR OF SOLID AND LIQUID FRACTIONS

Separation into solid and liquid fat was possible at 2 and 4°C. As expected, the amount of liquid fat fraction increased with increasing crystallization temperature (Fig. 1).

After 24 h of crystallization at 0°C, no liquid fraction was obtained after centrifugation. Temperatures between 4°C and 8.8°C can also be used to fractionate oil from yellow mealworm into solid and liquid fractions. Fractionation changed the color of the liquid and solid fractions (Fig. 2).
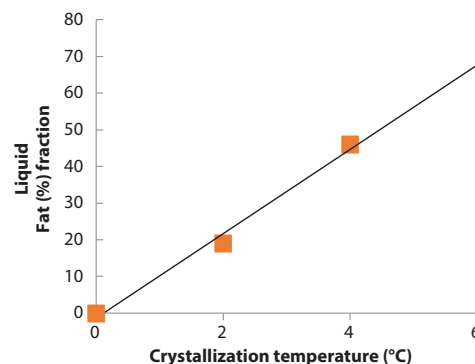
FIG. 1. Liquid fat fraction obtained after crystallization of yellow mealworm at 0, 1 and 4°C (y = 11.5x – 1.33, r2 = 0.99)

We analyzed the color of the unfractionated oil and the solid and liquid fractions using a Hunter Lab colorimeter in L*a*b* scale. In general, the color of the solid fractions was more red-yellow in color as compared with the liquid fractions (Table 1). The liquid fraction had a bright appearance, and the red and yellow tones were lower in the liquid oil fractionated at 2°C, in comparison with oil separated at 4°C.

CRYSTALLIZATION AND MELTING RANGE OF THE FRACTIONATED OIL

Thermal analysis was performed using a TA Q1000 differential scanning calorimeter (DSC) (New Castle, DE) calibrated with indium. Non-isothermal analysis was used to study the ther-

TABLE 1. Color of the liquid and solid fat fractions of Tenebrio molitor, measured at 20°C. L*a*b* scale was used. The data shown is the average of two repetitions.

Sample	L*	a*	b*
Unfractionated oil	15.72	1.35	12.86
Solid fraction 4°C	34.27	3.26	25.33
Solid fraction 2°C	21.01	3.14	18.97
Liquid fraction 4°C	5.12	0.15	2.81
Liquid fraction 2°C	4.40	-0.56	1.74

mal behavior of the oil and its fractions. The non-isothermal conditions were as follows: The oil was heated to 70°C for 10 min to remove all crystals. The oil was cooled at 5°C/min from 70 to -60°C, then stored at -60°C for 10 min. Next, the melting behavior was determined by heating at 5°C/min from the -60 to 60°C. The maximum point of the exotherms and endotherms were considered as the crystallization point and melting point, respectively.

The unfractionated oil of yellow meal worm showed four crystallization points (-45.4, -19.9, -5, and 3.6°C) and three melting points (-24.7, -17.4, and 16.7°C) (Table 2). The liquid fractions lacked the two highest crystallization points (-5 and 3.6°C), and the last melting point was reduced from 16.7°C to 1.7 and 3.2°C (L4 and L2, respectively). The solid fractions lacked the crystallization point at -5°C and showed an increase in the highest crystallization points from 3.6 to up to 10.7°C (S4 and S2, respectively). The final melting point of the solid fractions was increased from 16.7 to 21.5 and 27.1°C (S2 and S4, respectively).
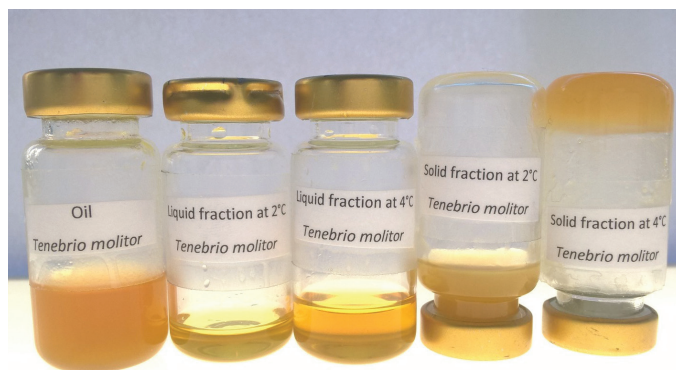
FIG. 2. Unfractionated and fractionated yellow meal worm oil. This picture was taken after stabilizing the oil for 2 h at 24°C (S4—solid fraction at 4°C; S2—solid fraction at 2°C; L4—liquid fraction at 4°C; L2—liquid fraction at 2°C; YMW— unfractionated oil)

FATTY ACID COMPOSITION OF THE FRACTIONATED OIL

The FA composition of the unfractionated oil and its fraction was determined by GC-FID (ISO15885:2002/IDF184:2002). Similar FA composition of the unfractionated oil was found in previous works done in our laboratory (Tzompa-Sosa *et al.*, 2014). It is interesting that the FA composition between the unfractionated oil and its fractions did not show large variations. Therefore, differences in the physical properties of the fractions cannot be explained by their FA composition. To understand the differences in physical properties seen in this study, it will be necessary to understand the kinetics of crystallization and the TAG profile and structure of the oil and its fractions.

A WIDE SPECTRUM OF PHYSICAL PROPERTIES

After fractionation, the solid and the liquid fraction did show differences in color and physical appearance When the fractions were kept at room temperature (24°C), the solid fraction obtained after fractionation at 4°C was a hard fat, similar to that of a margarine whereas the solid fraction obtained after

TABLE 2. Crystallization and melting points of unfractionated and fractionated yellow mealworm oil (N=2)

Sample	Crystallization points				Melting Points		
YMW	-45.4	-19.9	-5.0	3.6	-24.7	-17.4	16.7
S4	-46.3	-19.3	10.7	-	-24.4	-18.0	27.1
S2	-46.3	-19.8	2.7	-	-24.4	-16.9	21.5
L4	-49.4	-19.7		-	-25.5	-18.3	1.7
L2	-44.7	-19.5	-	-	-24.3	-17.4	3.2

fractionation at 2°C was semi-solid (Fig. 2). The liquid fractions obtained after fractionation were both in a liquid state and had a bright and transparent appearance, which is typical for a table oil.

The solid fractions obtained after fractionation showed crystallization and melting peaks at low temperatures (< -19°C). This can partially be explained by the lack of differences seen in the FA composition among the unfractionated oil and its fractions (Table 3). It is possible to obtain larger differences if the fractionation process is improved by either changing the fractionation temperatures or by using different methods of

TABLE 3. Fatty acid composition (g/100g of fat) of unfractionated and fractionated yellow mealworm oil (N=2)

FA	Unfractionated oil	Fractionated			
		Solid 2°C	Solid 4°C	Liquid 2°C	Liquid 4°C
C-10:0	0.01			0.01	0.01
C-12:0	0.14	0.13	0.14	0.14	0.14
C-13:0	0.04	0.04	0.04	0.04	0.04
C-14:0	2.20	2.19	2.20	2.19	2.19
C-14:1 cis 9	0.02	0.02	0.02	0.02	0.02
C-15:0 iso	-	0.01	0.01	0.01	0.01
C-15:0 anteiso	0.03	0.03	0.03	0.03	0.03
C-15:0	0.16	0.16	0.17	0.16	0.16
C-16:0	15.06	15.14	15.21	14.92	14.94
C-16:1 trans 9	0.61	0.60	0.62	0.63	0.62
C-16:1 cis 9	1.70	1.68	1.68	1.72	1.71
C-17:0 iso	0.02	0.03	0.02	0.02	0.02
C-17:0 anteiso	0.02	0.02	0.02	0.02	0.02
C-17:0	0.18	0.18	0.18	0.17	0.18
C-17:1 cis 9	0.21	0.21	0.21	0.21	0.21
C-16:3 cis 7,10,13 (HTA) ω-3	0.03	0.03	0.03	0.03	0.03
C-18:0	3.13	3.24	3.31	3.01	3.03
C-18:1 trans 10	0.05	0.02	0.04	0.02	0.03
C-18:1 trans 11	-	-	-	0.03	0.03
C-18:1 cis 9	38.06	37.79	37.55	38.49	38.50
C-18:1 cis 11	0.58	0.54	0.57	0.57	0.56
C-18:1 cis 12	0.02	0.01	0.01	0.02	0.02

fractionation, such as press filtration (Timms, 2005). Nevertheless, the fractionation process presented in this work succeeded in changing the physical properties of yellow mealworm oil. And we showed that the physical properties of yellow mealworm oil can be changed by dry fractionation. This can broaden the applications of this oil as a food ingredient.

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	Unfractionated oil	Fractionated			
FA		Solid 2°C	Solid 4°C	Liquid 2°C	Liquid 4°C
C-18:2 cis 9,12 (LA) ω-6	29.46	29.27	29.14	29.68	29.70
C-18:3 cis 6,9,12 (GLA) ω-6	1.45	1.27	1.39	1.45	1.43
C-18:3 cis 9,12,15 (ALA) ω-3	1.64	1.63	1.62	1.66	1.66
C-18:2 cis 9, trans 11	0.03	0.14	0.12	0.05	0.05
C-20:0	0.09	0.10	0.10	0.08	0.09
C-21:0 / C-20:2 cis 11,14 (EDA)	0.07	0.07	0.07	0.08	0.07
C-20:3 cis 8,11,14 (DGLA) ω-6	-	-	0.16	-	-
C-20:4 cis 5,8,11,14 (ARA)	0.02	0.01	0.02	-	-
C-22:0	0.16	0.30	0.15	0.14	0.14
C-22:4 cis 7,10,13,16 (AA) ω-6	0.05	0.08	0.06	0.05	0.05
C-24:0	0.04	0.20	0.15	-	-
C-24:1 cis 15	-	-	-	0.03	0.02
C-22:6 cis 4,7,10,13,16,19 (DHA) ω-3	0.01	0.01	-	-	0.01
C-24:4 cis 9,12,15,18 (TTA)	0.02	0.02	0.02	0.02	0.03
Total CLA	<0.10	<0.10	0.13	0.14	<0.10
Total ω-3	1.68	1.66	1.65	1.69	1.71
Total ω-6	30.96	30.63	30.75	31.19	31.18
ω-6/ω-3 ratio	18.43	18.45	18.64	18.46	18.23
Total SFA	21.35	21.05	21.80	21.85	21.00
Total UFA	73.98	73.36	73.28	74.72	74.70
Total MUFA	41.23	40.87	40.70	41.73	41.70
Total PUFA	32.71	32.45	32.54	32.94	32.96

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AOCS 2016 award recipients

AOCS celebrates ingenuity and collaboration by honoring those individuals and teams who have taken the industry to the next level, who have advanced the quality and depth of the profession, and who have leveraged their knowledge for the benefit of the society. These individuals from around the world were recognized during the 107th AOCS Annual Meeting and Expo (AM&E) held May 1–4, 2016, in Salt Lake City, Utah, USA. The September issue of *Inform* will include highlights from the science presented at the meeting.

SOCIETY AWARDS

AWARD OF MERIT

DILIP K. NAKHASI, Senior Director, Research & Development, Stratas Foods LCC, USA. The award recognizes leadership in technical, administrative, or special committees and activities; outstanding service that has advanced the Society's prestige, standing, or interests.

Nakhasi has contributed to the success of the Society through over a decade of committee work and Division leadership. He has devoted much time within the Edible Applications Technology Division, having served on the leadership team as Chairperson, as Vice Chairperson, and on award committees.

He has also been very active with Society meetings by helping to organize the programming of previous Annual Meetings, and he has a long history of involvement with the Division Council. During his leadership, the EAT Division has grown its technical program to include six solid technical sessions at the annual meeting.

Currently, Nakhasi is volunteering as the Program Committee chairperson, while also focusing his time on the mentoring of AOCS' younger members and preparing them for increased participation within the Society.

As stated by a colleague in one of his nomination letters, "Few AOCS members have contributed more to the AOCS Divisions than Dilip Nakhasi, and he has consistently done so without desire or search for recognition." His long and dedicated service to our Society is noted with this award.

FELLOW AWARD

Five AOCS Fellows were inducted at the AM&E. They join a select group of veteran AOCS members achievements in science entitle them to exceptional recognition, or who have rendered unusually important service to the Society or to the profession. The five are James A. Kenar, Leonard M. Sidisky, Eric A. Decker, Tong Wang, and Thomas A. McKeon.

JAMES A. KENAR, Research Scientist for the US Department of Agriculture, Agricultural Research Service, National Center for Agricultural Utilization Research, USA, is a prominent fats and oils researcher, well-versed in techniques necessary for the synthesis, purification, characterization, and scale-up of organic agricultural compounds, and a world-recognized expert in the fields of oleochemicals and industrials oils. He is also an influential writer, with many of his publications being featured in the industry's top peer-reviewed journals.

Kenar has been an AOCS member for 17 years, during which he has been active in committee work, Industrial Oil Products Division leadership, and as a contributor and Associate Editor for AOCS' *Journal of the American Oil Chemists' Society (JAOCS)*. He became Editor-in-Chief of *JAOCS* in May 2016. He has long contributed his time and expertise to the advancement of the Society, and his appointment as a Fellow duly recognizes these years of service.

LEONARD M. SIDISKY, R&D Manager for the Gas Separations Business Unit at Supelco, a member of the Sigma-Aldrich Group, USA, is responsible for having developed many novel technologies related to gas chromatography, solidphase microextraction, and high-performance carbon adsorbents. He is a world-renowned lecturer and an authority in the fields of gas chromatography and lipid analysis. His work at the forefront of emerging fats and oils related sciences and technologies has resulted in numerous applications for the food and industrial sectors. A presenter of papers and seminars worldwide, Sidisky has published over 25 journal articles in the industry's most prestigious peer-reviewed journals.

Sidisky has been an AOCS member for 26 years and is very active in the Analytical Division, the Northeast Section leadership, and the leadership of the Technical Steering Committee. He has also served on the AOCS Governing Board as member-at-large since 2010, and is the recipient of several prestigious AOCS awards. In countless ways over the past decades, he has leveraged his expertise and influence in the fats and oils industries to ensure the growth and advancement of AOCS.

ERIC A. DECKER, Department Head, Department of Food Science at the University of Massachusetts Amherst, USA, is known globally for his expertise in the field of lipid chemistry. The recipient of numerous prestigious honors and awards over the years, he has contributed to the science and technology of fats and oils with the publication of over 300 journal articles, 27 book chapters, and the securing of 10 patents in his field. He continues to have a meaningful impact on commercial products that rely on emulsions and oxidative stability of lipids in food, and his research has been critical to the success of many commercial products. Even with those notable contributions, perhaps his most lasting contribution to the fats and oils sciences has been the training of 22 doctoral and 19 masters' degree students who are now active members of AOCS and who are advancing the science of lipids at top universities and industry-leading companies around the world.

Decker has been an AOCS member for over 15 years and has made many direct contributions to the Society as a leader and a volunteer. Along with his service on the AOCS Governing Board as a member-at-large, Decker has contributed heavily to AOCS publications as a committee member and chair of the Content Value Center and through the submission of many articles to AOCS journals.

TONG WANG, Professor, Department of Food Science and Human Nutrition, Iowa State University, USA, is a leading researcher in the fields of lipid chemistry, phosphatides, proteins, and biofuels. With over 120 articles published in industry-leading journals and eight patents to her name, she is widely sought after as an international lecturer, author, and journal reviewer. Her work as a scientist, author, and professor have netted her an impressive collection of awards and honors, all of which confirm her prominence as a researcher in lipid chemistry and associated fields.

Wang has been a member of AOCS for 21 years and is very active in the Phospholipid Division, where she has served as Chairperson, Vice Chairperson, and Secretary-Treasurer. Wang has also contributed to the growth of AOCS' publications through her many years of work on the Publications Steering Committee and as an Associate Editor of *JAOCS*.

THOMAS A. McKEON, Research Chemist, United States Department of Agriculture, Agricultural Research Service, Western Regional Research Center, USA, works in the field of lipid biochemistry, where his work has notably corrected several prevalent misunderstandings regarding fatty acid biosynthesis in plants, the role of oleoyl-12-hydroxlyase in ricinoleic acid synthesis, and others. His groundbreaking research and other unique contributions to the science of lipid chemistry have led him to be a much sought-after lecturer and journal reviewer.

McKeon has been an AOCS member for 19 years, and has contributed to the growth of the Biotechnology Division through his service as Chairperson, Vice Chairperson, and Secretary-Treasurer. He also has a notable history of service on the Books and Special Publications Committee, where his understanding of the leading-edge issues related to fats and oils chemistry has enhanced the quality of AOCS' publications. He has excelled in academia, is a top researcher in his field, and works actively to promote educational opportunities for younger scientists.

SCIENTIFIC AWARDS

SUPELCO/NICHOLAS PELICK—
AOCS RESEARCH AWARD
$10,000 honorarium, $1,500 travel stipend, and a plaque

The Supelco/Nicholas Pelick–AOCS Research Award is for accomplishment of outstanding original research in fats, oils, lipid chemistry, or biochemistry, the results of which have been presented through publication of technical papers. The award is funded by Supelco Inc., a subsidiary of Sigma-Aldrich, and Nicholas Pelick, an AOCS past president.

D. JULIAN McCLEMENTS, Professor, Department of Food Science, University of Massachusetts Amherst, USA, is renowned worldwide for advancing how the industry understands the structuring of lipids used in food applications. His work has led to dramatic improvements in quality, chemical stability, and functionality of lipids in a large variety of complex food matrices. McClements has published over 600 peer-reviewed papers and 11 books, the importance and groundbreaking nature of which is widely acknowledged by the scientific 2016 community. He is regarded as an international authority in the fields of Food Science and Emulsion Science. McClements has received numerous awards and honors, including the Babcock-Hart Award (IFT, 2015), Hilditch Memorial Award (SCI, 2012), Marcel Loncin Research Prize (IFT, 2010), Stephen S. Chang Award (AOCS, 2010), and the Research and Development Award (IFT, 2007); and he is a Fellow in several professional societies (IFT, 2015, ACS, 2015, RSC, 2014).

STEPHEN S. CHANG AWARD
$1,500 honorarium and a jade horse

The Stephen S. Chang Award recognizes a scientist, technologist, or engineer who has conducted distinguished basic research that has been used by industry for the improvement or development of products related to lipids. The award was endowed by the late Stephen S. Chang and his wife, Lucy D. Chang.

JOHN L. HARWOOD, Professor, School of Biosciences, Cardiff University, Canada, is one of the leading scientists and researchers in biochemistry and lipid science. His research on thiocarbamates, pyridazinones, ethofumesate, and graminicides received widespread support from many industrial collaborators, and this work led to the determination of the mechanisms of action of these herbicides and pesticides. Through over 590 published articles and a number of authored books, students, researchers, and biochemists around the world rely on him as an important resource. As detailed in one of his nomination letters, "John's career and achievements can be presented as an ideal model of how fundamental science can dramatically impact industrial products, processes, and importance." Another letter said, "Dr. Harwood's contributions to lipid science over the course of his career has been extraordinary. More than 600 scientific contributions, including a vast number of published scientific articles and several books, and numerous prestigious awards are a testimony to his success." Some of these awards and honors include being formally recognized in 2014 with the Chevreul Award of the Société française pour l'étude des lipides (SFEL), the 2016 Morton Lecture Award by the Biochemical Society, and as a distinguished Fellow of AOCS (2014).

GEORGE SCHROEPFER MEDAL
$5,000 honorarium.and bronze medal

The George Schroepfer Medal recognizes significant and distinguished accomplishments in the steroid field, defined to encompass sterols and other natural synthetic compounds incorporating the tetracyclic gonane ring system. The award was endowed by colleagues and friends of the late George J. Schroepfer, Jr., a leader in the sterol and lipid field for more than 40 years.

STEVEN L. KELLY, Professor, Institute of Life Science and College of Medicine, Swansea University, Wales, UK, has been a leader in the sterol field for more than 30 years. Some of his notable contributions to the fields of sterols and biochemistry include developing a systematic approach to unearth the molecular libraries that code and regulate ergosterol metabolome in microbes. Furthermore, his studies regarding the mode of action and resistance to azole antifungals, and how these mixed-function oxidase enzymes have mutations in their primary structure which are associated with drug resistance, have led the industry to a better understanding of the relationship between sterol biosynthesis and pathogenicity. His understanding of biochemistry and genetics of enzymes in eukaryotic cells required for cholesterol and other sterol biosynthesis truly sets him apart as a leader in his field. As one of his nomination letters states, "Dr. Kelly's research regarding the lethality of CYP1 inhibitors when found in fungi and yeast, and how these organisms cause deadly infections in humans, has directly led to groundbreaking advances in medicine and drug development." Kelly's research accomplishments have made him a much sought after speaker at international mycological/antifungal and actinomycete related symposia, in addition to an impressive range of international biochemistry conferences. Furthermore, he is a contributing author to over 180 peer-reviewed articles, and numerous other papers. As another nominee letter states, "If I were to name one leader in the biochemistry of drugs and drug resistance in pathogenic fungi, it would be Dr. Kelly. His work in the pathogenic fungi has had a huge impact on the field of drug activity and drug resistance."

DIVISION AWARDS

ANALYTICAL DIVISION:
HERBERT J. DUTTON AWARD
$1,000 honorarium, $1,000 travel stipend, and a plaque

The award is presented for significant contribution to the analysis of fats and oils or to improvement in the understanding of the processes used in the fats and oils industries. The award is named for Dr. Dutton, a long-time research leader at the US Department of Agriculture facility in Peoria, Illinois, USA.

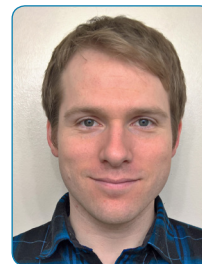**PIERLUIGI DELMONTE**, US Food & Drug Administration, USA

Student Award
RYAN WEST, Ryerson University, Canada
WEI XIA, Dalhousie University, Canada

Delmonte   **West**   **Xia**

BIOTECHNOLOGY DIVISION
Student Award
JUNKI MIYAMOTO, Hiroshima University, Japan
MOLLY J. SPROSTON, University of Georgia, USA
TAEHOON KIM, Korea University, Republic of Korea

EDIBLE APPLICATIONS TECHNOLOGY DIVISION: TIMOTHY L. MOUNTS AWARD
$750 honorarium and a plaque

The award is for either basic or applied research accomplishments relating to the science, technology, or application of edible oils in food products. It memorializes the former AOCS president, who was a distinguished research scientist with the US Department of Agriculture. The award is sponsored by Bunge North America.

KI-TEAK LEE, Chungham National University, Republic of Korea

Student Award
SHY KAI NG, Universiti Putra Malaysia, Malaysia

HEALTH AND NUTRITION DIVISION: RALPH HOLMAN LIFETIME ACHIEVEMENT AWARD
$500 honorarium, $1,000 travel stipend, and an orchid print

The award recognizes outstanding performance and meritorious contributions to the health and nutrition interest area. The award is named after Ralph Holman in recognition of his lifetime service to the study of essential fatty acids.

Ng

CAROL LAMMI-KEEFE, Louisiana State University, USA

Student Award
IFEANYI NWACHUKWU, University of Manitoba, Canada

SURFACTANTS AND DETERGENTS DIVISION: SAMUEL ROSEN MEMORIAL AWARD
$2,000 honorarium and a plaque

The award recognizes a significant advance in, or application of, the principles of surfactant chemistry by a chemist working in the industry. The award is sponsored by Milton Rosen in honor of his father, Samuel, who worked as an industrial chemist on the formulation of printing inks for more than four decades.
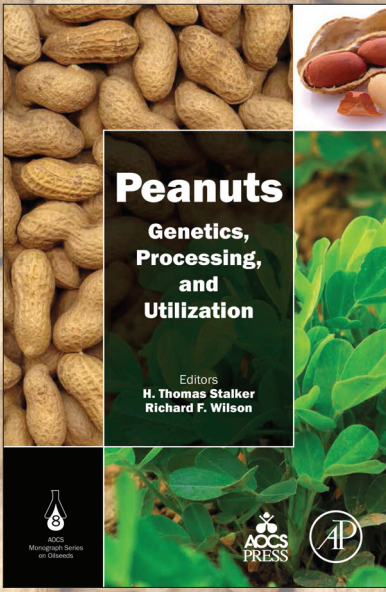
DENNIS S. MURPHY, Stepan Company, USA

Student Award
FAN WANG, University of Guelph, Canada

Nwachukwu

Murphy

STUDENT RECOGNITION

THOMAS H. SMOUSE MEMORIAL FELLOWSHIP AWARD
$10,000 scholarship, $5,000 research funding, and bookends

DAVID JOHNSON, University of Massachusetts Amherst, USA

The Archer Daniels Midland Foundation, the AOCS, the AOCS Foundation, and the family and friends of Dr. Smouse have established and assisted in funding a fellowship program designed to encourage and support outstanding graduate research in a field of study consistent with the areas of interest to the AOCS.

Johnson

RALPH H. POTTS MEMORIAL FELLOWSHIP AWARD
$2,000 scholarship, travel stipend, and a plaque

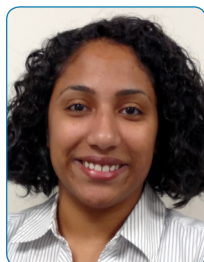*The Ralph H. Potts Award is presented annually to a graduate student working in the chemistry of fats and oils and their derivatives. The award is sponsored by AkzoNobel to memorialize Ralph Potts, a pioneer in research on industrial uses of fatty acids.*

MAXINE J. ROMAN, University of Massachusetts Amherst, USA

Roman

AOCS FOUNDATION HONORED STUDENT AWARDS
Travel stipend and a certificate

The award recognizes graduate students at any institution of higher learning who are conducting research in any area of science dealing with fats and lipids and who are interested in the areas of science and technology. Supported by contributions from members as well as companies in the industry.

IFEANYI NWACHUKWU, University of Manitoba, Canada
MAXINE J. ROMAN, University of Massachusetts Amherst, USA (Manuchehr Eijadi Award)
SARA SHINN, University of Arkansas, USA (Peter and Clare G. Kalustian Award)
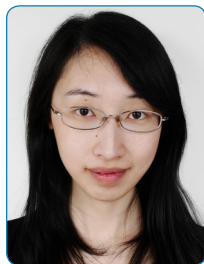**WEI WEI**, Aarhus University, Denmark

Shinn

MANUCHEHR (MANNY) EIJADI AWARD
$1,000 scholarship and a certificate

The Eijadi Award recognizes outstanding merit and performance by an AOCS Honored Student. The award, established by Mr. Eijadi, is intended to help the recipient finance his or her studies.

MAXINE J. ROMAN, University of Massachusetts Amherst, USA

Wei

Critical mass from UMass

Faculty and students from the University of Massachusetts, Amherst, were exceptionally prominent at this year's Awards Plenary and AOCS Business Meeting, where they took home one AOCS Fellow Award, the Supelco/Nicholas Pelick–AOCS Research Award, and four of the most prestigious student awards, including the Thomas Smouse Fellowship, the Manuchehr Ejadi Award, the Ralph Potts Memorial Fellowship, and the Hans Kaunitz award.

The graduate program in the Department of Food Science at the University of Massachusetts was ranked #1 by the US National Research Council, the research arm of the National Academies of Sciences, Engineering, and Medicine. What makes them such a powerhouse? An understanding of food at the molecular level and strong partnerships with industry. Watch video at https://www.youtube.com/watch?v=9CEHyDI5UMQ.

PETER AND CLARE KALUSTIAN AWARD
$1,000 scholarship and a certificate

The Kalustian Award recognizes outstanding merit and performance by an AOCS Honored Student. The award is supported by the Kalustian estate.

SARA SHINN, University of Arkansas, USA

BEST PAPER AWARDS

ADM/PROTEIN AND CO-PRODUCTS DIVISION
BEST PAPER CHEMISTRY/NUTRITION
Validation of a Method for Quantitation of Soybean Lectin in Commercial Varieties (*JAOCS 92*(8): 1085–1092).
Matthew L. Breeze, Elisa Leyva-Guerrero, Grant R. Yeaman, Yelena Dudin, Ryan Akel, Phil Brune, Fred Claussen, Cecil Dharmasri, Jenny Golbach, and nine others

ENGINEERING/TECHNOLOGY
Examination of the Causes of Instability of Soy Protein Isolate During Storage Through Probing of the Heat Induced Aggregation (*JAOCS 92*(8): 1075–1084).
Feng Xian Guo, Youling L. Xiong, Fang Qin, Hua-Jun Jian, Xiao-Lin Huang, and Jie Chen

ACI DISTINGUISHED PAPER AWARD
Using the Scanning Fluid Dynamic Gauging Device to Understand the Cleaning of Baked Lard Soiling Layer (*JSD 18*(6): 933–947).
Akin Ali, Zayeed Alam, Glenn Ward, and D. Ian Wilson

EDWIN FRANKEL FOR BEST PAPER IN LIPID OXIDATION AND QUALITY
New Analytical Evidence of Discontinuous Oxidation in Dried Microencapsulated Lipids (*JAOCS 92*(11-12): 1601–1607).
Arturo Morales, Susana Marmesat, Mª Victoria Ruiz- Méndez, Gloria Márquez-Ruiz, Joaquín Velasco.

ADDITIONAL AWARDS

ALTON E. BAILEY AWARD
$750 honorarium and a plaque

The award recognizes outstanding research and exceptional service in the field of lipids and associated products. The medal commemorates Alton E. Bailey's great contributions to the field of fats and oils as a researcher, as an author of several standard books in the field, and as a leader in the work of the Society. Archer Daniels Midland Company Inc. sponsor the award.

Ahmad

MOGHIS U. AHMAD, Jina Pharmaceuticals Inc., USA

HANS KAUNITZ AWARD
$1,000 honorarium, $500 travel allowance, and a certificate

The award recognizes the outstanding performance and merit of a graduate student within the United States.

CANSU E. GUMUS, University of Massachusetts Amherst, USA

Gumus

AOCS MEETING WATCH

October 4–7, 2016. World Conference on Fabric and Home Care—Singapore 2016, Shangri-La Hotel, Singapore. http://singapore.aocs.org

April 30–May 3, 2017. AOCS Annual Meeting and Industry Showcases, Rosen Shingle Creek, Orlando, Florida, USA. http://annualmeeting.aocs.org

September 11–14, 2017. 17th AOCS Latin American Congress and Exhibition on Fats and Oils, Grand Fiesta Americana Coral Beach Hotel, Cancun, Mexico.

For in-depth details on these and other upcoming meetings, visit http://aocs.org/meetings or contact the AOCS Meetings Department (email: meetings@aocs.org; phone: +1 217-693-4821; fax: +1 217-693-4865).
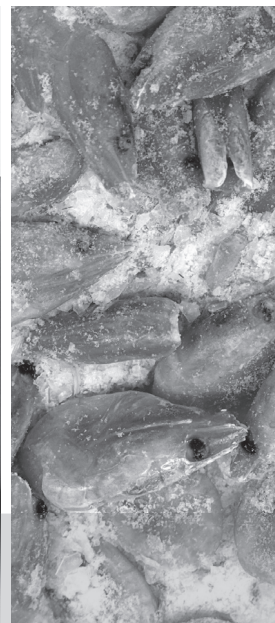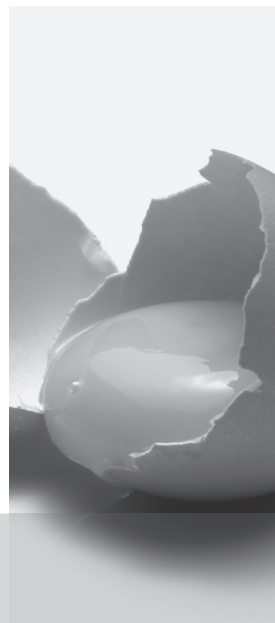
Should the **food industry** fund **nutrition research?**

Olio is an Inform *column that highlights research, issues, trends, and technologies of interest to the oils and fats community.*

Laura Cassiday

In recent months, several scientific journals and media outlets have spotlighted the sometimes murky topic of industry-funded nutrition research. At the heart of the issue is conflict of interest: When a researcher accepts money from a food company to conduct a particular research project, does he or she become (consciously or sub-consciously) beholden to deliver results favorable to that company? Critics argue that every industry-funded study is by definition tainted by bias or corruption, whereas proponents claim that many important research questions have been answered only through the sustenance of food industry dollars. Meanwhile, consumers are confused as to whether they can trust the latest news story that claims walnuts, milk, avocados, chocolate, or GMOs are healthful, considering the self-interested nature of the funding sources.

In the January 2016 issue of *JAMA Internal Medicine*, Marion Nestle, professor of nutrition and food studies at New York University, authored a Viewpoint entitled, "Corporate funding of food and nutrition research: science or marketing?" (http://doi.org/10.1001/jamainternmed.2015.6667). In the piece, Nestle (who, by the way, is no relation to the Nestlé food company) mentions an informal analysis she conducted of studies funded by food and beverage companies. Between March and October 2015, Nestle identified 76 industry-funded studies, of which 70 reported results favorable to the sponsor's interests. According to Nestle's Food Politics blog (http://www.foodpolitics.com), as of March 2016, the tally had risen to 166 industry-funded nutrition studies, with 154 reporting favorable results. Nestle admits that her analysis was not systematic, being confined only to "journals I happen to be reading" and studies contributed by readers of her blog. Therefore, her own results are likely susceptible to some forms of bias; nonetheless, the overwhelming positivity of the industry-funded studies is striking.

And Nestle's findings are not unprecedented. In 2007, researchers led by Lenard Lesser at Children's Hospital in Boston, Massachusetts, USA, conducted a systematic study of the relationship between funding source and conclusion in nutrition-related scientific articles (http://doi.org/10.1371/journal.pmed.0040005). The researchers confined their study to 206 articles about soft drinks, juice, and milk published between January 1, 1999, and December 31, 2003. They found that beverage-related articles funded entirely by industry were four to eight times more likely to be favorable to the financial interests of the sponsors than those lacking industry funding.

There are several possible explanations for why the results of industry-funded studies should be so overwhelmingly in favor of the sponsor's views. Only the most cynical of critics would contend that researchers are deliberately manipulating data to support their sponsors. Although this may happen, it is probably rare because in most cases, the peer review process would detect such blatant fraud. If bias exists, it is likely more subtle: A researcher (consciously or subconsciously) overstates positive or neutral conclusions, while downplaying or omitting negative results. Perhaps in some cases, an industry-funded researcher would be discouraged from publishing data contrary to the company's views.

Although such situations likely exist, they have not been well documented. "It would certainly be helpful, if not essential, for Dr. Nestle or others to show that industry-funded studies have more design flaws, inappropriate analyses, or unjustified conclusions relative to similar studies funded by other sources," writes Richard Kahn of the University of

North Carolina School of Medicine in a Comment & Response to Nestle's Viewpoint (http://doi.org/10.1001/jamaint-ernmed.2016.0906, 2016). In the absence of such data, an association between funding source and conclusions cannot in itself prove bias.

Another explanation may be the choice of projects funded by industry. A company is more likely to contribute money to likeminded researchers or to projects that are expected to support their viewpoints. For example, *The New York Times* recently published an investigative report on Coca-Cola's funding of academic researchers who promote physical activity as a more effective means of preventing obesity than counting calories (such as in sugary sodas) (O'Connor, A., http://tinyurl.com/soda-studies, 2015). Mars, Inc. has funded studies on the beneficial effects of cocoa flavanols on blood pressure and arterial function. The company has used these results to advertise its products, despite the fact that most cocoa fla-vanols are destroyed during chocolate processing (Nestle, M., http://doi.org/10.1001/jamainternmed.2015.6667, 2016). "The study investigators, one of whom is employed by Mars, followed well-established scientific protocols in conducting the research," writes Nestle. "Science is not the issue here. Marketing is the issue."

But proponents of industry-funded research argue that without corporate resources, many important research questions in both basic and applied science would remain unanswered. "Collaboration with industry has allowed me to discover things that I could not have found otherwise," writes Martijn B. Katan, professor of nutrition at Vrije Universiteit, in Amsterdam, the Netherlands (http://doi.org/10.1371/journal.pmed.0040006, 2007). "We discovered the effects of trans fatty acids on heart disease risk thanks to the expertise of Unilever, and the cholesterol-raising factor in unfiltered coffee thanks to Nestle."

"Providing safeguards are in place, no reasonable person should doubt the integrity of collaborative research," argue Paul Aveyard and Derek Yach in a *BMJ* perspective (http://doi.org/10.1136/bmj.i2161, 2016). Suggested safeguards include

the following: The researcher, not the company, should design, conduct, and analyze the study; the scientist should have no commercial interest in the product; payments should be made to the organization and not the researcher; payments should cover only the cost of the research; analyses should be conducted by independent statisticians; and researchers should publish the results regardless of outcome.

To maintain the integrity of the scientific process, researchers must consciously guard against bias, not only of a financial nature, but also biases related to preconceived notions, career considerations, pet theories, or even political agendas. In addition, researchers should avoid hyping results or allowing food companies to misrepresent their findings to sell a product. To prevent blanket condemnation of industry-funded studies, scientists and the media must better educate the public on how to critically evaluate scientific studies on a case-by-case basis, rather than just assuming that all industry-funded research is inherently flawed, or conversely, trustworthy. In this regard, the role of the public information officer and reporter in issuing and relaying press releases is not to be understated. Along with better explanations of results, the methods by which they were obtained, and their significance, press releases and news stories should clearly state the funding sources and any caveats of the study.

Olio is produced by Inform's associate editor, Laura Cassiday. She can be contacted at laura.cassiday@aocs.org.

Information

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Katan, M. B. (2007) "Does industry sponsorship undermine the integrity of nutrition research?" *PLoS Med. 4*, e6. http://doi.org/10.1371/journal.pmed.0040006

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O'Connor, A. (2015) "Coca-Cola funds scientists who shift blame for obesity away from bad diets." *The New York Times*, August 9, 2015. http://tinyurl.com/soda-studies

The **big** preservatives "crisis"

Regulatory Review is a regular column featuring updates on regulatory matters concerning oils- and fats-related industries.

Vanessa Zainzinger

The cosmetics industry says a series of bans and restrictions, over the past two years, have curbed its ability to develop effective formulations, to protect products from fungi and bacteria. This is to a point where companies are alarmed about the future of their products. But the hazards and risks associated with this class of chemicals make adequately protecting human health, while satisfying consumer expectations for cosmetics which last long enough on the shelves, a challenge, industry says.

Bans and restrictions on widely used substances have come into force over the last two years. Propylparaben and butylparaben were banned from some leave-on products, and restricted in all cosmetics. The transitional period for selling off existing stocks ended in October last year. Five more parabens—isopropylparaben, isobutylparaben, phenylparaben, benzylparaben, and pentylparaben—were banned in all cosmetic products. And the mixture of methylchloroisothiazolinone and methylisothiazolinone (MCI/MI) has been banned from leave-on products, since July 2015. It is restricted in rinse-off products to a maximum concentration of 0.0015%.

More preservatives bans and restrictions are in the pipeline in 2016, such as methylisothiazolinone, polyaminopropyl biguanide (PHMB), and chloroacetamide.

"INSUFFICIENT DIVERSITY"

But with each additional ban or restriction, the cosmetics industry loses more of its ability to innovate and formulate new products, according to director general of trade body Cosmetics Europe, John Chave. A total of 58 preservatives are currently permitted for use."

Cosmed, the French cosmetics association for SMEs, says the choice of a preservative depends to a large extent on the formula itself, and its optimal efficiency. "Every preservative

could be more or less effective against specific germs. Hence, it is crucial to maintain a diverse palette of preservatives to cover the multiple categories of products and microbes," says Cosmed's head of regulatory affairs, Aline Weber.

Additionally, there are very few new preservatives—if any—being developed, the associations say. This is largely blamed on the marketing ban on cosmetic products, containing animal-tested ingredients, which was introduced under the EU Cosmetics Regulation. The ban is limiting industry's ability to develop and test new preservatives, because alternative safety testing methods are not available for some endpoints, says Weber. As a result, she says, "a lack of information is hindering the [European Commission's] scientific committees from concluding on the safety of some ingredients."

According to Chave, the cosmetics industry agrees that maintaining a wide palette of preservatives is one of the key challenges for the cosmetics sector: "This is a crisis. Everybody in the industry recognizes that this is a genuine, serious problem, and we know that we can't afford to be passive on this— we have to be proactive."

Cosmetics industry associations in Europe have, together, begun to tackle the problem. Cosmetics Europe, the trade body with the broadest reach, is developing a product preservation strategy this year, with the aim of addressing the big

issues behind the preservatives crisis: regulation and consumer perception.

THE REGULATORY PROBLEM

The main regulatory text, responsible for ensuring cosmetics on the European market are safe, is the cosmetics regulation. But this is not the core of the problem, according to Chave. It is the way various regulations interact in the EU which needs a rethink.

A posterchild for this problem is polyaminopropyl biguanide (PHMB). The substance was classified under the classification, labelling and packaging (CLP) Regulation as carcinogenic, mutagenic and reprotoxic (CMR) category 2. The classification applied from 1 January 2015.

However, the cosmetics regulation allows CMR 2 substances to be used in cosmetic products if deemed safe by the European Commission's Scientific Committee for Consumer Safety (SCCS).

"The way the cosmetics regulation is set up means we have an opportunity to defend our ingredients," Chave says. "But the view taken by the member states was that [a CMR 2 classification] means the substance is automatically prohibited."

Monitoring projects by the Danish Consumer Council's Think Chemicals initiative, last year, flagged up PHMB in creams, make-up removers and cleansing tissues. According to the council, the substance is clearly banned and companies should be asked to withdraw PHMB-containing products from the market and be penalized if they don't comply.

A 2014 assessment by the SCCS concluded that PHMB is not safe when used at a maximum concentration of 0.3% but mentioned that "safe usage could result from a lower use concentration" or restrictions to product categories.

Industry is working on a proposal to the European Commission, which could ensure that the substance remains on the authorized list, Chave says.

Further down the line, Cosmetics Europe hopes the Commission will "rethink how regulations interact in the EU."

At the Commission's industry directorate, DG Grow, the industry's concerns have not fallen on deaf ears. The regulators say they recognize the preservatives crisis as "one of the key challenges to the cosmetics sector."

"Each additional loss or restriction of a preservative may lead to a possible shortage of preservatives, which could increase consumers' risk of sensitization to the remaining authorized preservatives," an official says.

"Having a larger spectrum of preservatives could reduce the risk of exposing consumers to just a few of these ingredients, thereby decreasing the incidence of allergies and sensitization."

The Commission stands behind the risk management process for cosmetic ingredients, and the assessments carried out by the SCCS, which it calls "independent" and "of high value to the cosmetics sector." It says it also takes into account the input provided by member states and industry to "ensure a high level of protection of human health and a functioning of the internal market."

Human health NGOs, such as Breast Cancer UK, were pleased to see the Commission take action on parabens. The charity's chemicals and policy officer, Margaret Wexler, says most of its concerns center on endocrine disrupting chemicals (EDCs). This made oestrogenic parabens, which have been found in breast milk and breast tissue, a priority.

"Things are definitely improving," says Wexler. "The EU cosmetics Regulation and REACH have been very positive. And once the EDC criteria are sorted out, things will start moving more quickly."

Breast Cancer UK hopes the Commission will tackle triclosan next. The preservative is currently being phased out in human hygiene disinfectants, such as soaps and hand washes, after it found no support for authorization under the biocidal products Regulation (BPR). It is still allowed for use in cosmetic products at concentrations up to 0.3%.

"The fact is that [triclosan] has been banned [under the BPR] because it is toxic to aquatic organisms, but it is also implicated in ovarian cancer. It's not logical to keep it in cosmetics," Wexler says.

CHEMOPHOBIA

The preservatives crisis is a multifaceted problem. Consumer awareness of the chemicals they are exposed to has risen, and preservatives have taken a hit, says Breast Cancer UK.

"People are becoming more aware of the number of chemicals present [in cosmetics], not just because more and more charities work in the area, but also because it is a topic shown a lot more in the media now than it was five years ago," says Wexler.

This has not been lost on industry. Chave acknowledges that the word "preservative" now implies something potentially threatening, "an unnatural intervention in the way of the world."
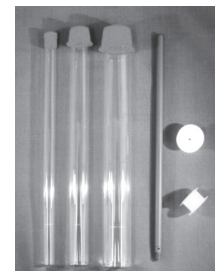
Argentina: high oleic sunflower oil (HO-SFO) for **trans-fats replacement**

Leslie Kleiner

On December 2014, Argentina started restricting the levels of trans fatty acids in foods to 5% of all fat used in food, and 2% for oils, fats, and margarines. In 2015, the US Food and Drug Administration (FDA) announced the removal of the GRAS status for partially hydrogenated oil (PHO), and consequent phase out of PHO as a food ingredient. The FDA ruling further accentuated the need to find solutions for trans-fats replacement in foods, and Argentina, as well as its neighboring countries, have been using high-oleic sunflower oil (HO SFO) for that purpose. To learn more about this topic, I interviewed Eduardo Dubinsky, partner at DM Consultants, ex-president of ASAGA (Argentine Society of Fats and Oils) and of LA-AOCS (Latin American Section of AOCS).

Latin America Update is a regular Inform *column that features information about fats, oils, and related materials in that region.*

Q: **When did HO-SFO start to be implemented as a solution for trans-fats replacement in Argentina?**

The process of using HO-SFO for partial hydrogenated oil replacement in Argentina, started in the year 2000. However, at this time the country was experiencing a severe economic crisis in which new developments for health and nutrition were not top priority. It was during the year 2004 that many large food companies in Argentina started to perform full or partial substitution of partially hydrogenated oils by HO-SFO.

Q: **What were the major challenges when replacing partially hydrogenated oils by HO-SFO?**

Originally, modified oils were not easily accepted as solutions for the replacement of partially hydrogenated oils in bakery applications, because there was the misconception

that liquid oils could not replace the functionality of solid fats in some bakery applications. However, we discovered that HO-SFO can be successfully used in industrial breads, crackers, cookies, and biscuits, among other applications. It wasn't until the adverse effects of trans fats were noted, that this technology became more widely implemented by companies interested in eliminating trans fats from their products. Another challenge was HO-SFO's use as frying oil, due to some studies in which it was reported that a low (7–10%) linolenic acid content led to differences in flavor that were perceived negatively by consumers. However, vigorous testing in large companies, such as PepsiCo, McCain, and McDonald's in Argentina, led to the replacement of trans fats for HO-SFO in fried products, by the year 2006.

Q: **What are some of the most important limitations of high-oleic oils in terms of using them to fully replace trans fats without increasing saturates?**

A limitation is that some applications, such as puff pastries, fillings, and coatings, do require a minimum level of saturated fats. Therefore, our consultancy also led for another customer, the development of processes for the production and then food application of another type of sunflower oil with high-stearic and high-oleic traits. Although the results have been outstanding, these traits are not a cost-effective alternative at this time, because of current lower crop yields and lower fat content in the grain, compared with conventional-, mid-, and high-oleic sunflower varieties.

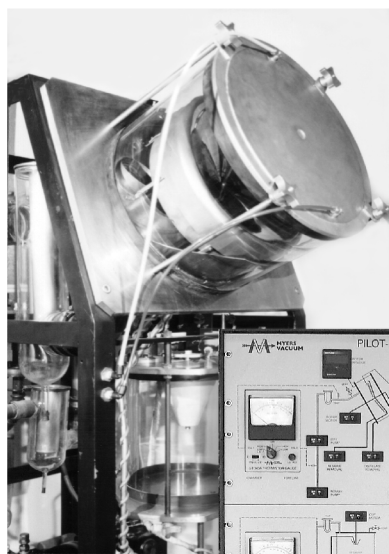**Q:** **What is the future of high-oleic oils?**

The use of high-oleic oils has been growing steadily, with the most popular being sunflower and canola. However, there are also other high-oleic varieties arising from peanut, safflower, and, most recently, palm oil. A relatively new

development on high-oleic oils is that of high-oleic soybean oil (HO-SBO), which is expected to grow exponentially in the next five years. HO-SBO is one of the main alternatives for the replacement of trans fats in the United States, and will likely continue to grow in regions where GMO's (genetically modified organisms) are not a concern.

Q: **What are the main innovations that we could expect for next years?**

With regulatory, nutritional, and environmental trends as important market drivers, we could expect the need for not only the replacement of trans fats, but also of a significant reduction of saturates (as in palm oil). One of the main issues is then to have different ways of structuring variable quantities of liquid oils depending on the food application. Currently, the most widespread processes rely on the combination of chemical or enzymatic interesterification with full hydrogenation. However, these processes still involve a significant level of saturates. In that sense, there are currently commercially available novel alternatives based on oil-in-water emulsion technology that mimic solid shortening behavior. High-oleic sunflower oil, given its oxidative stability, could be an excellent raw material for these novel product, and in this way could provide a desirable combination of nutrition profile, functionality, and shelf life.

Latin America Update is produced by Leslie Kleiner, R&D Project Coordinator in Confectionery Applications at Roquette Americas Inc., Geneva, Illinois, USA, and a contributing editor of *Inform*. She can be reached at LESLIE.KLEINER@roquette.com.

PATENTS

Reducing astringency in compositions containing phenolic compounds

Bortlik, K., *et al.*, Nestec SA, US9265276, February 23, 2016

The present invention in general relates to the field of taste. In particular it relates to the reduction of astringency. One embodiment of the present invention relates to the use of at least one phospholipid for the preparation of a phenol containing composition to reduce the astringency of the composition.

Epoxy acid thermoset resins and composites that can be hot-fashioned and recycled

Leibler, L., *et al.*, Centre National De La Recherche Scientifique and Arkema, US9266292, February 23, 2016

Resins and thermoset composites comprising them, these materials being able to be hot-fashioned. These compositions resulting from placing at least one thermosetting resin precursor, this thermosetting resin precursor comprising hydroxyl functions and/or epoxy groups, and optionally ester functions, in contact with at least one hardener chosen from carboxylic acids, in the presence of at least one transesterification catalyst whose total molar amount is between 5 percent and 25 percent of the total molar amount of hydroxyl and epoxy contained in the thermosetting resin precursor. Process for manufacturing these materials, process for transforming and process for recycling these materials. New solid forms of resins and of thermoset composites that may be used in the implementation of these processes.

Coating composition and method for the protection of complex metal structures and components used in submerged environments

Fink, T.G., *et al.*, Oxifree Holdings Corp., US9267040, February 23, 2016

A coating composition for application to a subsea component or structure has cellulose acetate an amount of approximately 47 percent by weight of the total composition, diisooctyl phthalate in an amount of approximately 17 percent by weight of the total composition, a fatty acid ester in an amount of approximately 23 percent by weight of the total composition, a vegetable oil in an amount of approximately 8 percent by weight of the total composition, a stabilizer and a silica amorphous in which the stabilizer and the silica amorphous are in amount of approximately 5 percent by weight of the total composition. The stabilizer can be either titanium dioxide or aluminum dioxide. The vegetable oil is canola oil.

Crystal growth inhibitor for fats and oils

Kato, H., *et al.*, US9271512, Taiyo Kagaku Co., Ltd., March 1, 2016

An inhibitor for crystal growth of fats and oils, containing a polyglycerol fatty acid ester, which is an esterified product formed between a polyglycerol and a fatty acid, the polyglycerol having a hydroxyl value of 850 mg KOH/g or less and a ratio of primary hydroxyl groups to all the hydroxyl groups of the polyglycerol of 50 percent or more, wherein the polyglycerol fatty acid ester has a hydroxyl value of 100 mg KOH/g or less. Since the inhibitor for crystal growth of fats and oils of the present invention can inhibit crystal growth of fats and oils by adding the inhibitor to fats and oils, storage property of the fats and oils in a refrigerator, cold climates, or the like, so that the inhibitor can be suitably used in liquid fats and oils such as salad oil for which transparency is important.

Composition comprising a sucrose ester and a polyglycerol ester

Poletti, M., *et al.*, L'Oreal US9272165, March 1, 2016

Composition containing an aqueous phase, a lipophilic compound and an emulsifying system containing a fatty acid ester of sucrose and a fatty acid ester of polyglycerol, and to its use in the cosmetics field, in particular for cleansing and/or for removing makeup from keratin materials.

Solvent-based coating compositions

Li, C., *et al.*, Akzo Nobel Coatings International B.V., US9273226, March 1, 2016

Coating compositions are disclosed. In some embodiments, the coating compositions are used to coat substrates such as packaging materials and the like for the storage of food and beverages. The coating compositions can be prepared by reacting an epoxidized vegetable oil and a hydroxyl functional material in the presence of an acid catalyst to form a hydroxyl functional oil polyol, mixing the hydroxyl functional oil polyol (with or without epoxidized polybutadiene) with a functional polyolefin copolymer to form a mixture, reacting the mixture with an ethylenically unsaturated monomer component in the presence of an initiator to form a graft copolymer, and crosslinking the graft copolymer with a crosslinker to form the coating composition.

Human breast milk lipid mimetic as dietary supplement

Meiri-Bendek, I., *et al.*, Enzymotec Ltd., US9282748, March 15, 2016

Disclosed is an enzymatically prepared fat base composition comprising a mixture of vegetable-derived triglycerides, characterized in that it has a total palmitic acid residues content of at most 38 percent of the total fatty acid residues, and in that at least 60 percent, preferably 62 percent of the fatty acid moieties at the sn-2 position of the glycerol backbone are palmitic acid residues, at least 70 percent of the fatty acid moieties at the sn-1 and sn-3 positions of the glycerol backbone are unsaturated, at least 40 percent, pref-

erably 40–60 percent, of the unsaturated fatty acid moieties at the sn-i and sn-3 positions are oleic acid moieties and at least 6 percent, preferably 6-17 percent, of the unsaturated fatty acid moieties at the sn-1 and sn-3 positions are linoleic acid moieties, its preparation and its various uses in the field of infant formulas.

Use of a fatty acid composition comprising at least one of EPA and DHA or any combinations thereof

Bryhn, M., *et al.*, Pronova Biopharma Norge AS, US9282760, March 15, 2016

A method is disclosed for treatment and prevention of obesity, an overweight condition or for controlling body weight reduction, wherein an effective amount of a fatty acid composition comprising at least one of (all-Z omega-3)-5,8,11,14,17-eicosapentaenoic acid (EPA) and (all-Z omega-3)-4,7,10,13,16,19-docosahexaenoic acid (DHA) or any combinations thereof, is administered to a human or an animal. Additionally, a dietary product is disclosed, containing a fatty acid composition comprising at least one of EPA and DHA or any combinations thereof, for non-medical treatment of obesity, an overweight condition and/or for supporting and controlling body weight reduction. Finally, a method is disclosed for supplementing a dietary product with a fatty acid composition mentioned above.

Conveyor-based frying apparatus and methods of use

Hockett W.T., *et al.*, Conagra Foods Lamb Weston, Inc., US9282852, March 15, 2016

A fryer can include a base having a reservoir for receiving oil for frying a food product and a hood coupled to the base. The fryer can have an inlet at an upstream section and an outlet at a downstream section. At least one conveyor can move food product from the inlet to the outlet. A first baffle member and second baffle member can be positioned over the conveyor to define a frying chamber therebetween. The first and second baffle members can restrict air from flowing into the frying chamber from outside of the frying chamber.

Pharmaceutical compositions for local administration

Panzner, S., *et al.*, Marina Biotech Inc., US9283186, March 15, 2016

A pharmaceutical composition for local application is disclosed, said composition comprising a nucleic acid as a therapeutic agent, an excipient and a pharmaceutically acceptable vehicle therefor, said excipient comprising a liposome. The excipient comprises an amphoteric liposome having an isoelectric point between 4 and 7.4 and said composition is formulated to have a pH in the range 3 to 5. The composition may administered in the form of a colloidal suspension and may be buffered to the lower pH at the time of use by the addition of a suitable acidifying means to a substantially neutral suspension of the nucleic acid and excipient that may be more suitable for long-term storage of the composition. Alternatively, the composition may be lyophi-

lised at the lower pH for subsequent reconstitution just prior to use with a suitable aqueous medium, such for example as substantially unbuffered water or saline.

Methods and compositions for improving cognitive function

French, S., *et al.*, Mars, Inc., US9283203, March 15, 2016

This invention relates to compositions, and methods of use thereof, for (i) enhancing executive cognitive function(s) (for example, decision making, planning, working memory, multitasking, judgment, numerical problem-solving, reading comprehension), and/or (ii) increasing blood flow in brain vasculature, comprising administering to a subject in need thereof, certain polyphenols such as flavanols, procyanidins, or pharmaceutically acceptable salts or derivatives thereof.

Disinfectant detergent composition

Wakita, K., *et al.*, NOF Corp., US9288977, March 22, 2016

A disinfectant detergent composition containing a food or food additive as a main component is provided. The disinfectant detergent composition contains the following components (a), (b), and (c). The sum [a+b] of the component (a) content and the component (b) content of the composition ranges from 0.1 percent to 30 percent by mass, the mass ratio [a/b] of the component (a) to the component (b) ranges from 1/2 to 4/1, and the component (c) content of the composition ranges from 60 percent to 99.5 percent by mass. (a) polyoxyethylene sorbitan monolaurate (b) a fatty acid glyceride in which the number of carbon atoms of its acyl group ranges from 8 to 12, the monoglyceride content of the component (b) being 85 percent by mass or more, the mass fraction of 1-monoglyceride relative to the total amount of monoglycerides being in the range of 0.9 to 1.0 (c) water and/or ethanol.

Thermal methods for treating a metathesis feedstock

Uptain, K.D., *et al.*, Elevance Renewable Sciences, Inc., US9284515, March 15, 2016

Various methods are provided for metathesizing a feedstock. In one aspect, a method includes providing a feedstock comprising a natural oil, heating the feedstock to a temperature greater than 100 degrees centigrade in the absence of oxygen, holding the feedstock at the temperature for a time sufficient to diminish catalyst poisons in the feedstock, and, following the heating and holding, combining a metathesis catalyst with the feedstock under conditions sufficient to metathesize the feedstock.

EXTRACTS & DISTILLATES

Micronutrients in vegetable oils: the impact of crushing and refining processes on vitamins and antioxidants in sunflower, rapeseed, and soybean oils

Tocopherols, phytosterols, polyphenols, and coenzymes Q are naturally present in oilseeds such as sunflower, rape, and soybean. Besides contributing to taste and color, micronutrients help protect against health disorders such as cardiovascular diseases and cancer. However, during the conventional oil manufacturing process, many minor components are lost. Given that diet is a major cause of cardiovascular diseases and cancer, it makes sense to optimize the content of micronutrients in food, and specifically in vegetable oils. These micronutrients have antioxidant properties that inhibit the oxidation of low-density lipoprotein cholesterol. This review summarizes important recent research emphasizing the impact of crushing and refining processes on the micronutrient content of different vegetable oils. After the crushing step, the total sterol content was high in crude rape, sunflower, and soybean oils, at 4358–10 569, 2212–4146, and 1735–4328 mg/kg, respectively. The tocopherol content was lower, at 464–1458, 725–1892, and 1094–2484 mg/kg, respectively, and the level of phenolics was 113–629, 10–120, and 23–148 mg/kg, respectively. The refining process destroyed micronutrients: 10–36% loss of total tocopherols, 6–52% loss of total sterols, and 93–98% loss of polyphenols. Studies have focused on improving the extraction of tocopherols by alternative heating (microwave treatment, roasting, or steaming processes). These treatments improved tocopherol content, and extraction was faster and consumed less energy.

Simple method for high purity acylated steryl glucosides synthesis

The present work covers an important gap in the field of analytic standards synthesis of the plants minor component, the acyl steryl glucosides (ASG). A simple and powerful procedure that allows the synthesis of different ASG has been introduced. The regioselective acylation of steryl glucosides on the C–6–OH of the glucose was produced using sym-collidine and acyl chloride. The reaction was optimized analyzing the conditions to maximize the isolated yield of the monoacylated product.

Potential of tocotrienols in the prevention and therapy of Alzheimer's disease

Currently there is no cure for Alzheimer's disease (AD); clinical trials are underway to reduce amyloid generation and deposition, a neuropathological hallmark in brains of AD patients. While genetic factors and neuroinflammation contribute significantly to AD pathogenesis, whether increased cholesterol level is a causative factor or a result of AD is equivocal. Prenylation of proteins regulating neuronal functions requires mevalonate-derived farnesyl pyrophosphate (FPP) and geranylgeranyl pyrophosphate (GGPP). The observation that the levels of FPP and GGPP, but not that of cholesterol, are elevated in AD patients is consistent with the finding that statins, competitive inhibitors of 3-hydroxy-3-methylglutaryl coenzyme A (HMG CoA) reductase, reduce FPP and GGPP levels and amyloid β protein production in preclinical studies. Retrospective studies show inverse correlations between incidence of AD and the intake and serum levels of the HMG CoA reductase-suppressive tocotrienols; tocopherols show mixed results. Tocotrienols, but not tocopherols, block the processing and nuclear localization of sterol regulatory element binding protein-2, the transcriptional factor for HMG CoA reductase and FPP synthase, and enhance the degradation of HMG CoA reductase. Consequently, tocotrienols deplete the pool of FPP and GGPP and potentially blunt prenylation-dependent AD pathogenesis. The antiinflammatory activity of tocotrienols further contributes to their protection against AD. The mevalonate- and inflammation-suppressive activities of tocotrienols may represent those of an estimated 23,000 mevalonate-derived plant secondary metabolites called isoprenoids, many of which are neuroprotective. Tocotrienol-containing plant foods and tocotrienol derivatives and formulations with enhanced bioavailability may offer a novel approach in AD prevention and treatment.

Ruminant and industrial trans-fatty acid uptake in the heart

Dietary trans-fats are strongly associated with heart disease. However, the capacity for the tissues of the body, and specifically the heart, to take up trans-fats is unknown. It is also unknown if different trans-fats have different uptake capacities in the heart and other tissues of the body. Diets of low-density lipoprotein receptor-deficient mice were supplemented for 14 weeks with foods that contained 1.5% of the trans-fat elaidic acid or vaccenic acid. Tissues were extracted and frozen in liquid nitrogen, and then lipids were analyzed by gas chromatography for fatty acid content. Isolated cardiomyocytes were also exposed to elaidic or vaccenic acid in cell culture media for 24 h. Dietary supplementation with vaccenic or elaidic acid resulted in a 20-fold higher accumulation of these TFAs in fat deposits in the body in comparison to liver. Liver tissue accumulated about twice as much per gram tissue as heart. Similar quantities of both elaidic acid and vaccenic acid were taken up by the tissues. Isolated cardiomyocytes exhibited an unusually large uptake of trans-fat, and this was dependent upon both the concen-

tration and duration of exposure to the trans-fats but not upon the type of trans-fat. Expression levels of CD36 and FATP4 were not significantly changed during dietary interventions or exposure of cells to trans-fats. We conclude that fat, liver, and heart (including cardiomyocytes) are all capable of accumulating trans-fat in response to dietary supplementation without changes in fatty acid transport protein expression.

Rhamnolipid adsorption in soil: factors, unique features, and considerations for use as green antizoosporic agents

Dashtbozorg, S.S., *et al., J. Agric. Food Chem.* 64: 3330–3337, 2016, http://dx.doi.org/10.1021/acs.jafc.6b00215.

In aqueous solutions, rhamnolipids effectively kill the motile zoospores responsible for spreading many pathogens, including soy-infecting *Phytophthora sojae*. For use in soil, adsorption properties need to be considered. Having low critical micelle concentrations, rhamnolipids tend to form micelles/aggregates with unknown effects on soil adsorption. Effects of soil pH, rhamnolipid congener structure, and concentration were examined. Congeners were identified and each quantitated for adsorptive partitioning. The adsorption isotherm at pH 6.5 showed a multi-stage profile plateauing at 1700 μg/g of soil. Less hydrophilic congeners adsorbed preferentially: R-C10-C12 > R-C10-C12:1 > RR-C10-C12:1 > RR-C10-C12 > R-C10-C10 > RR-C10-C10 > R-C8-C10 > RR-C8-C10 (where R is rhamnose and C# is the carbon number of β-hydroxy fatty acid).

Adsorptive selectivity among congeners was very clear in dilute solutions but diminished with increasing concentrations. Results were interpreted with aggregate formation in solutions and on the soil surface. The cost estimate made accordingly supported the economic feasibility of rhamnolipid antizoosporic uses in soil.

Method development for the determination of free and esterified sterols in button mushrooms (*Agaricus bisporus*)

Hammann, S. and W. Vetter, *J. Agric. Food Chem.* 64: 3437–3444, 2016, http://dx.doi.org/10.1021/acs.jafc.6b00383.

Ergosterol is the major sterol in button mushrooms (*Agaricus bisporus*) and can occur as free alcohol or esterified with fatty acids (ergosteryl esters). In this study, gas chromatography with mass spectrometry in the selected ion monitoring mode (GC/MS-SIM) was used to determine ergosterol and ergosteryl esters as well as other sterols and steryl esters in button mushrooms. Different quality control measures were established and sample preparation procedures were compared to prevent the formation of artifacts and the degradation of ergosteryl esters. The final method was then used for the determination of ergosterol (443 ± 44 mg/100 g dry matter (d.m.)) and esterified ergosterol (12 ± 6 mg/100 g d.m.) in button mushroom samples (n = 4). While the free sterol fraction was vastly dominated by ergosterol (~90% of five sterols in total), the steryl ester fraction was more diversified (nine sterols in total, ergosterol ~55%) and consisted primarily of linoleic acid esters.

Analysis of alkylresorcinols in wheat germ oil and barley germ oil via HPLC and fluorescence detection: cochromatography with tocols

Moreau, R.A. and X. Fang, *Cereal Chem.* 93: 293–298, May/June 2016, http://dx.doi.org/10.1094/CCHEM-07-15-0141-R.

Alkylresorcinols are long-chain phenolic compounds that have been reported to be localized in the outer layers of the kernels of wheat, rye, barley, and other grains. A sensitive HPLC method with fluorescence detection was recently reported for the quantitative analysis of alkylresorcinols in cereal grains and products. Using this new HPLC method we report for the first time that wheat germ oil contains moderate levels of alkylresorcinols, approximately 800–1,500 µg per gram of oil. We also found that commercial wheat germ oil and some experimental samples of wheat germ oil and barley germ oil also contained three unknown peaks. Upon further evaluation of these peaks it was found that the peaks appeared to be tocopherols (one peak of α-tocopherol, one peak of δ-tocopherol, and a peak with the combination of β- and γ-tocopherol), even though the excitation and emission wavelengths for alkylresorcinols (excitation 274 nm and emission 300 nm) are different than those for tocols (excitation 294 nm and emission 326 nm). We also found that with this HPLC system one alkylresorcinol, AR17, had the same retention time (7.6 min) as δ-tocotrienol and that another alkylresorcinol, AR19, had the same retention time (10.8 min) as α-tocotrienol.

Property development of fatty acid methyl ester from waste coconut oil as engine fuel

Kalam, M.A., *et al.*, *Ind. Crops Prod.* 87: 333–339, September 2016, http://dx.doi.org/10.1016/j.indcrop.2016.04.021.

The properties, performance, and exhaust emissions of a four-cylinder indirect injection diesel engine fueled by FAME from waste coconut oil was evaluated in this study. Polymerization and carbon deposits on fuel-injector nozzles were also monitored. Ordinary diesel (OD) oil was used as a benchmark for comparison purposes. Tests included measuring high heating value, kinematic viscosity, specific density, cetane index, pour point, flash point, and Conradson carbon residue. Results showed that, the high calorific value decreased with increased coconut oil in coconut-oil blends. On average, the calorific value of all coconut-oil blends were about 6% lower than that of OD fuel. Density increased with increased coconut oil in coconut-oil blends because of the higher amount of carbon atoms in coconut-oil molecules. As a result, viscosity also increased with increased coconut oil in blends. Other properties of blended fuels varied according to their physicochemical properties. Results also showed that the brake power output of engine increased by about 5% when fueled by 30% coconut-oil-blended fuel. The average specific fuel consumption of coconut-oil-blended fuels increased by 7–10% compared with OD oil. The exhaust emissions of blended fuel were found to be much cleaner, containing less CO, HC, NOx, and smoke and benzene concentration. The coconut-oil-blended fuel also produced low particulate emission and carbon deposit on injector nozzles. For each coconut-oil-blended fuel, the engine did not have any starting difficulty and combus-

tion noise at >25 °C. The coconut-oil-based fuel also did not pose a severe environmental threat because of its low sulfur content.

Efficient and quantitative chemical transformation of vegetable oils to polyols through a thiol-ene reaction for thermoplastic polyurethanes

Alagi, P., *et al.*, *Ind. Crops Prod.* 87: 78–88, September 2016, http://dx.doi.org/10.1016/j.indcrop.2016.04.027.

Vegetable oils (VOs) such as castor oil and soybean oil were quantitatively transformed to polyols to afford industrially important thermoplastic polyurethanes (TPUs). Photoinduced thiol-ene click chemistry was investigated for the efficient preparation of VO based polyols with primary hydroxyl groups. To improve the reaction efficiency, experimental parameters, such as the concentration of the thiol compounds and reaction temperature, were carefully adjusted. For the first time, nearly complete and quantitative transformation of the carbon–carbon double bonds of the VOs to hydroxyl groups was achieved. The quantitative transformation of the carbon–carbon double bonds to hydroxyl groups allowed for the preparation of polyols with predetermined hydroxyl functionalities. The polyols were successfully incorporated into TPUs, affording elastomers with hyperbranched chain architectures. The TPUs exhibited high toughness along with excellent transparency and improved hysteresis behaviors under high deformation conditions. The study demonstrated efficient synthetic procedures for transforming sustainable plant resources to TPUs to modulate their mechanical and optical properties.

Kinetics of forming aldehydes in frying oils and their distribution in french fries revealed by LC–MS-based chemometrics

Wang, L., *et al.*, *J. Agric. Food Chem.* 64: 3881–3889, 2016, http://dx.doi.org/10.1021/acs.jafc.6b01127.

In this study, the kinetics of aldehyde formation in heated frying oils was characterized by 2-hydrazinoquinoline derivatization, liquid chromatography–mass spectrometry (LC–MS) analysis, principal component analysis (PCA), and hierarchical cluster analysis (HCA). The aldehydes contributing to time-dependent separation of heated soybean oil (HSO) in a PCA model were grouped by the HCA into three clusters (A1, A2, and B) on the basis of their kinetics and fatty acid precursors. The increases of 4-hydroxynonenal (4-HNE) and the A2-to-B ratio in HSO were well-correlated with the duration of thermal stress. Chemometric and quantitative analysis of three frying oils (soybean, corn, and canola oils) and French fry extracts further supported the associations between aldehyde profiles and fatty acid precursors and also revealed that the concentrations of pentanal, hexanal, acrolein, and the A2-to-B ratio in French fry extracts were more comparable to their values in the frying oils than other unsaturated aldehydes. All of these results suggest the roles of specific aldehydes or aldehyde clusters as novel markers of the lipid oxidation status for frying oils or fried foods.

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Attended the Annual Meeting May 1–4, 2016

Phase behavior of binary blends of four different waxes

Jana, S. and S. Martini, *J. Am. Oil Chem. Soc. 93*: 543–554, 2016, http://dx.doi.org/10.1007/s11746-016-2789-6.

The objective of this study was to investigate the phase behavior of binary blends of four waxes—beeswax (BW), paraffin wax (PW), sunflower wax (SFW), and rice bran wax (RBW)—using differential scanning calorimetry (DSC) and polarized light microscopy (PLM). Blends of BW/PW, RBW/PW, SFW/PW, SFW/RBW, SFW/BW, and RBW/BW were crystallized in a DSC, and their melting behavior was used to build binary phase diagrams. The microstructure of the crystalline networks formed in these blends was analyzed using PLM. BW/PW, SFW/PW, SFW/BW, and RBW/BW blends showed eutectic phase behavior, while RBW/SFW showed continuous solid solution and the RBW/PW blend showed monotectic behavior. Results from the box-counting fractal dimension (D_b) measurement of crystal morphology showed higher D_b values for the 20 and 80% wax blends, irrespective of crystallization temperature or wax type. D_b values of single waxes decrease as temperature increases.

Industrial Applications

Enzyme-assisted extraction processing from oilseeds: Principle, processing and application

Liu, J., *et al., Innov. Food Sci. Emerg. Technol. 35*: 184–193, June 2016, http://dx.doi.org/10.1016/j.ifset.2016.05.002.

Enzyme-assisted extraction processing (EAEP), feasible alternative to screw pressing and organic solvent extraction technologies, is a promising method for the simultaneous extraction of oil and protein from oilseed. This method incorporates comminuting, extraction buffers and enzymes to allow production of a range of oils and proteins although different challenges appear during the process. The demand for acceptable and high free oil yields and purities of protein is always incompatible in many processes. This review article covers technological aspects of EAEP, and discusses the application of enzymes in pretreatment, extraction and demulsification, and explores the quality characteristics and safety of the oils and proteins obtained, focusing particularly on recent application of EAEP at the laboratory and industrial scale. Industrial relevance: 1. Enzymes are widely used on an industrial scale but mainly as catalysts, and the applications mainly concerning the synthesis of pharmaceuticals, compounds for chemistry of specialty, polymers, etc. 2. At the industrial scale, one advantage of EAEP is environment benefit because it can avoid the risk of organic solvents and particularly hexane. 3. The quality of the products produced by the smooth process is usually higher. 4. EAEP technique is considered as an alternative method to produce valuable products without loss of quality at moderate conditions. 5. Compared with solvent extraction, EAEP is more eco-friendly. Besides that, one of the main advantages of EAEP is the specificity of enzymes.

Oilseed treatment by ultrasounds and microwaves to improve oil yield and quality: an overview

Koubaa , M., *et al., Food Res. Int. 85*: 59–66, July 2016, http://dx.doi.org/10.1016/j.foodres.2016.04.007.

Efficiency is a key point to ensure the profitability in the production of vegetable oils from oilseeds. To maximize the recovery yields of seed oils, the traditional process involves mechanical expression followed by subsequent chemical extraction using organic solvents (e.g. hexane). Besides health, environmental, and economic related issues to the use of organic solvents, thermal treatment of seeds during conventional oil extraction process inevitably leads to chemical changes (e.g. changes in macronutrients such as protein denaturation/degradation in the meal, oil oxidation, and changes in minor constituents such as fatty acids, sterols, phenolic compounds and tocols). Thus, at this stage of development there is a need for new efficient processes that can improve oil yield and its quality from an economical and environmental point of view. Several research groups have investigated the potential of ultrasounds (US) and microwaves (MW) as additional seed treatments to enhance oil yields and to reduce temperature and extraction times with promising results. The present review is devoted to critically discuss the main findings reported in the literature regarding the feasibility of using US and MW as potential tools to improve oil recovery yields as well as its nutritional, sensorial and physicochemical properties.

Extraction, characterization, purification and catalytic upgrading of algae lipids to fuel-like hydrocarbons

Santillan-Jimenez, E., *et al., Fuel 180*, 15: 668–678, September 2016, http://dx.doi.org/10.1016/j.fuel.2016.04.079.

The extraction, characterization, purification and upgrading of algal lipids was examined, utilizing *Scenedesmus acutus* microalgae grown with flue gas from a coal-fired power plant. Lipid extraction was achieved using a procedure based on the Bligh–Dyer method, modified so as to utilize a significantly decreased solvent:biomass ratio than the original protocol. Both activated carbon and K10 montmorillonite were found to function as efficient adsorbents for the removal of chlorophyll, phospholipids and sterols from the crude algae oil. The yield of purified lipids using this approach was similar to that obtained by in situ transesterification of the lipids in *S. acutus*, confirming that adsorption is an effective method for the removal of non-esterifiable lipids. During the deoxygenation of the purified algae oil at 260 °C over a Ni–Al layered double hydroxide catalyst, deactivation of the catalyst was observed, attributed to the presence of highly unsaturated lipid chains which can act as poisons by adsorbing strongly to the catalyst surface and/or acting as precursors to coke formation. However, upgrading at 300 °C gave better results, the liquid product consisting of ~99 wt% hydrocarbons, diesel-like (C10–C20) hydrocarbons constituting 76 wt% of the liquid after 4 h on stream.

Extracts & Distillates is compiled by Robert Moreau (US Department of Agriculture). Bryan Yeh (Intrexon) contributes references in the areas of industrial applications and synthetic biology.

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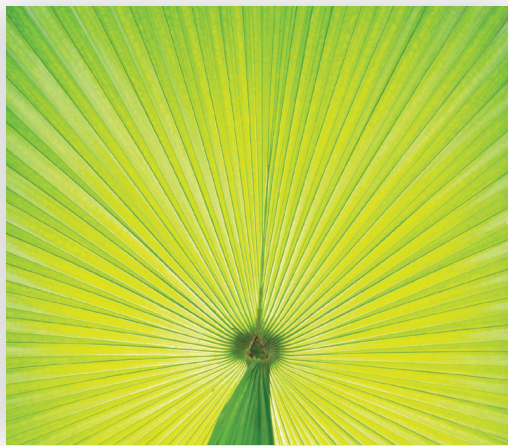
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