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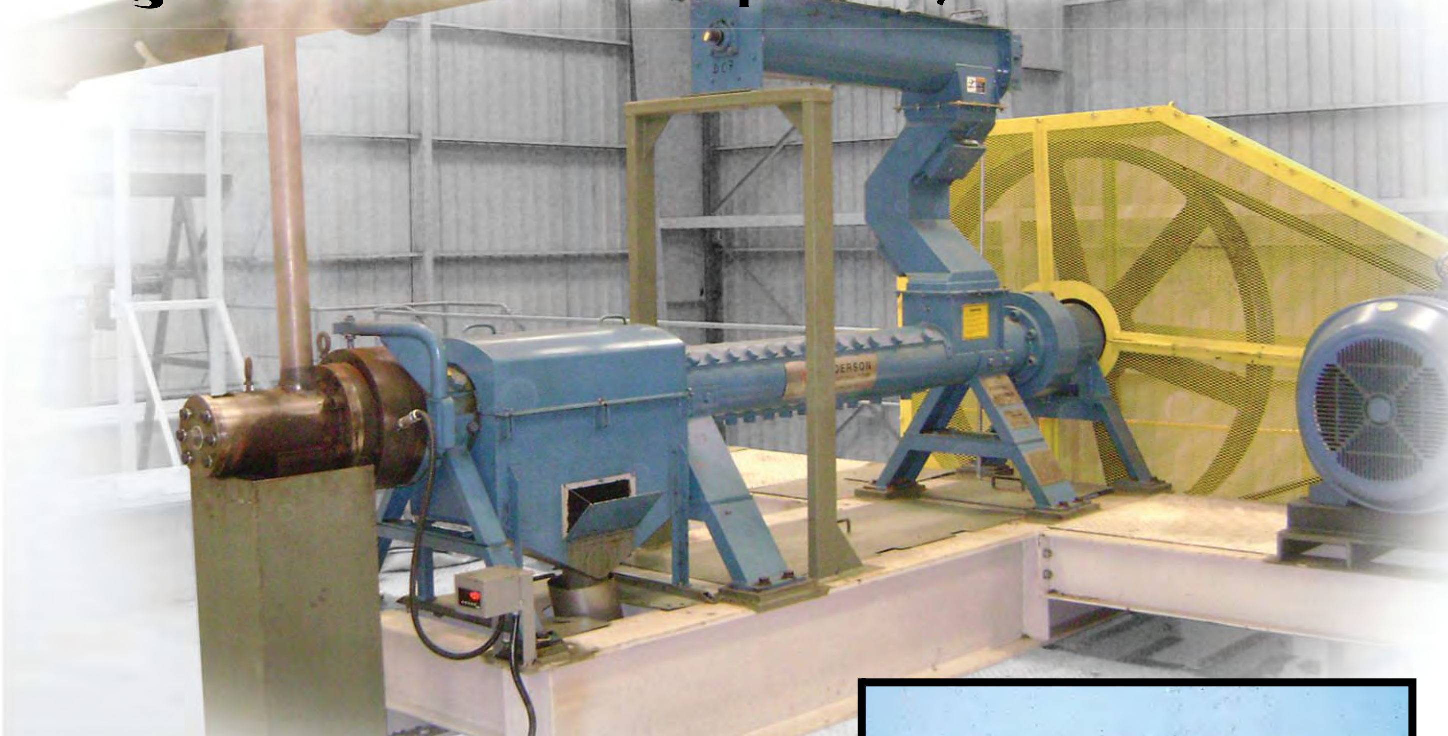

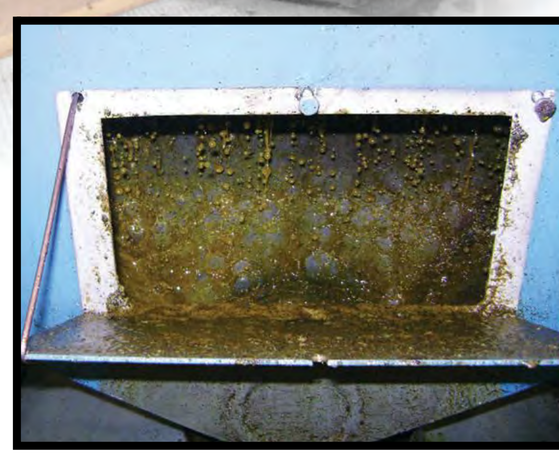

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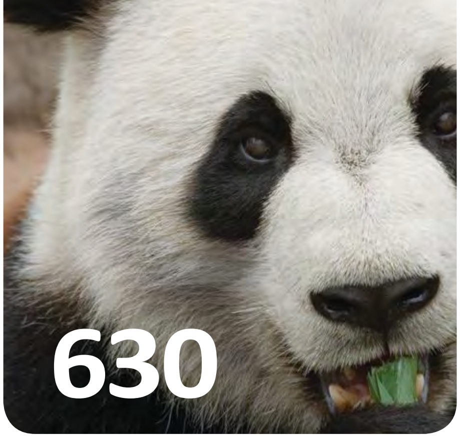

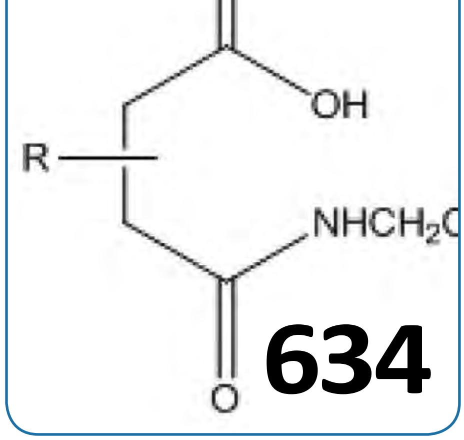

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ENHANCED OIL RECOVERY & HOUSEHOLD LAUNDRY—

more alike than you might think

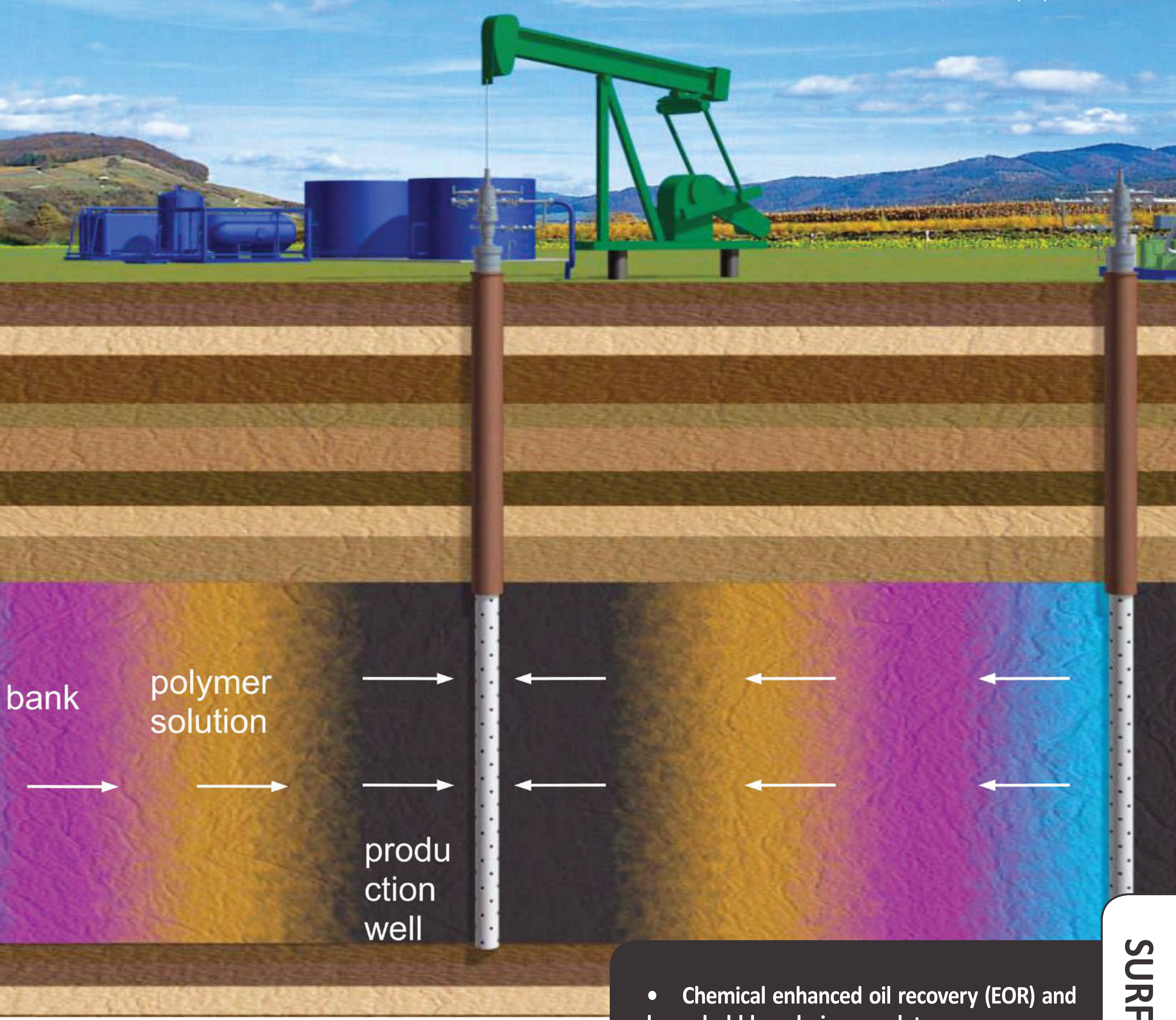
Kirk H. Raney

FIG. 1. Schematic of alkaline-surfactant-polymer oil recovery process.

Over the course of my career, I have worked on a variety of applications of surfactants, for both consumer and industrial uses. I have spent considerable time studying household laundry and chemical enhanced oil recovery (EOR) surfactants. On the surface, these are two very dissimilar uses of surfactants. However, I have also noted some striking similarities between them. As one use (i.e., household laundering) will continue to be a huge market for surfactants and the other (EOR) has tremendous growth potential and hence could compete for surfactant supply, I will describe some of these similarities, as well as some subtle differences, in this article.

This cover story is based on a presentation by Kirk H. Raney, winner of the 2013 Samuel Rosen Memorial Award given by AOCS in recognition of significant advancement, cumulative advancements, or application of the principles of surfactant chemistry.

Of primary importance when comparing household laundering and EOR is to recognize that both are aqueous-based detergency processes for "cleaning" porous media. Professor Milton Rosen has defined detergency in the following manner: "The term detergency, when applied to a surface-active agent, means the special property it has of enhancing the cleaning power of a liquid" (Rosen and Kunjappu, 2012). In home laundry, surfactant solutions are used to clean porous fabric substrates whereas aqueous surfactant slugs are used in chemical EOR to remove crude oil from porous rock such as sandstone or limestone.



• Chemical enhanced oil recovery (EOR) and household laundering are detergency processes that differ greatly in scale but share many similarities in mechanisms and technical requirements.

• The implementation onset of surfactant-based EOR projects will cause significant growth in surfactant consumption with some overlap and competition with laundry markets.

• The oil industry can learn much from the detergent industry with regard to surfactant product formulations, chemical logistics, environmental requirements, and legislation.

WHY CHEMICAL EOR?

During production of crude oil, 60–70% of the oil remains in the reservoir rock due to capillary forces, after conventional primary pressure-driven processes. In fact, up to 300 billion barrels of trapped oil are estimated to exist in the United States at this time (Henthorne, Walsh, and Llano, 2013). Future energy supply scenarios show that crude oil will continue to be the major source of the world's energy requirements, particularly for transportation. A recent study predicts that crude oil will still provide about one-quarter of the global energy demand in 2050 (Kramer and Haigh, 2009). Therefore, recovery of this

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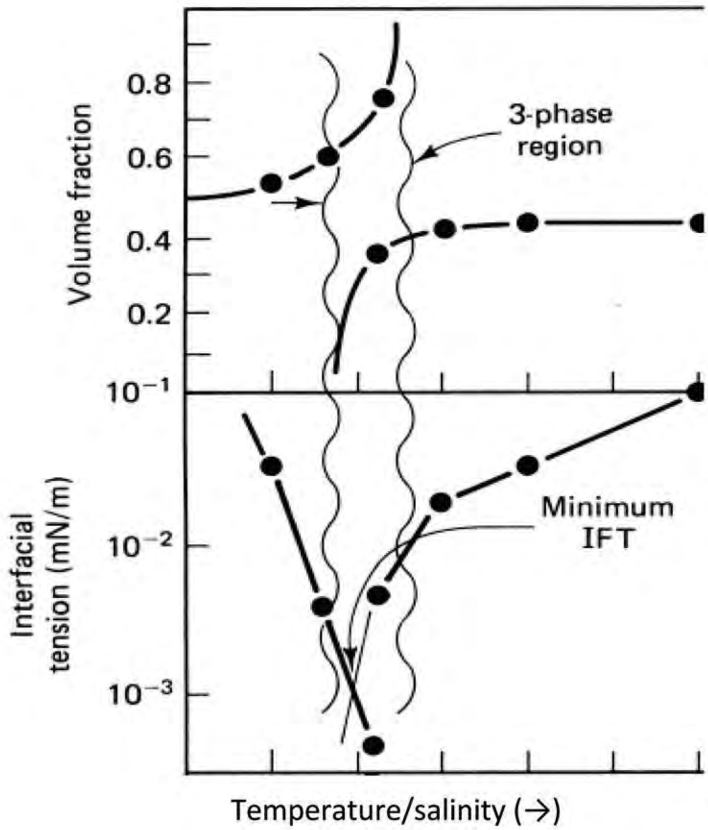

FIG. 2. Correlation of Winsor III phase behavior with ultralow oil-water interfacial tension (IFT) found at optimum salinity or the phase inversion temperature.

known trapped oil will be critical for several decades. Surfactant-based chemical EOR will be one way to recover some of this oil. Currently, there are about 40 surfactant-based EOR projects around the world, mostly at the pilot stage of production.

The alkaline-surfactant-polymer (ASP) EOR process works by pushing a slug of ASP "cocktail" through the reservoir rock, effectively "cleaning the rock" of valuable crude oil as it flows through it. The surfactant plays the key role of releasing the oil from the rock pores, while the alkalinity (in this case, sodium carbonate) protects the surfactant from water hardness ions, produces soap from the crude oil, and minimizes surfactant adsorption on the rock. The polymer, typically a hydrolyzed high-molecular-weight polyacrylamide, provides viscosity to the ASP slug to prevent fingering of the ASP solution through the oil and maintain plug flow and efficient oil displacement in the reservoir. Figure 1 (page 615) is a schematic diagram showing the flow of ASP fluids and the formation of an oil bank in the oil reservoir.

Due to the large pore volume of the reservoirs containing the trapped crude oil, a single chemical EOR application of 100,000 barrels injected/day would require about 100 million pounds (45,000 metric tons) of surfactant/year for several years. This amount of surfactant for one ASP flood is 2–3% of the approximately four billion pounds (1.8 million metric tons) of surfactants consumed annually for

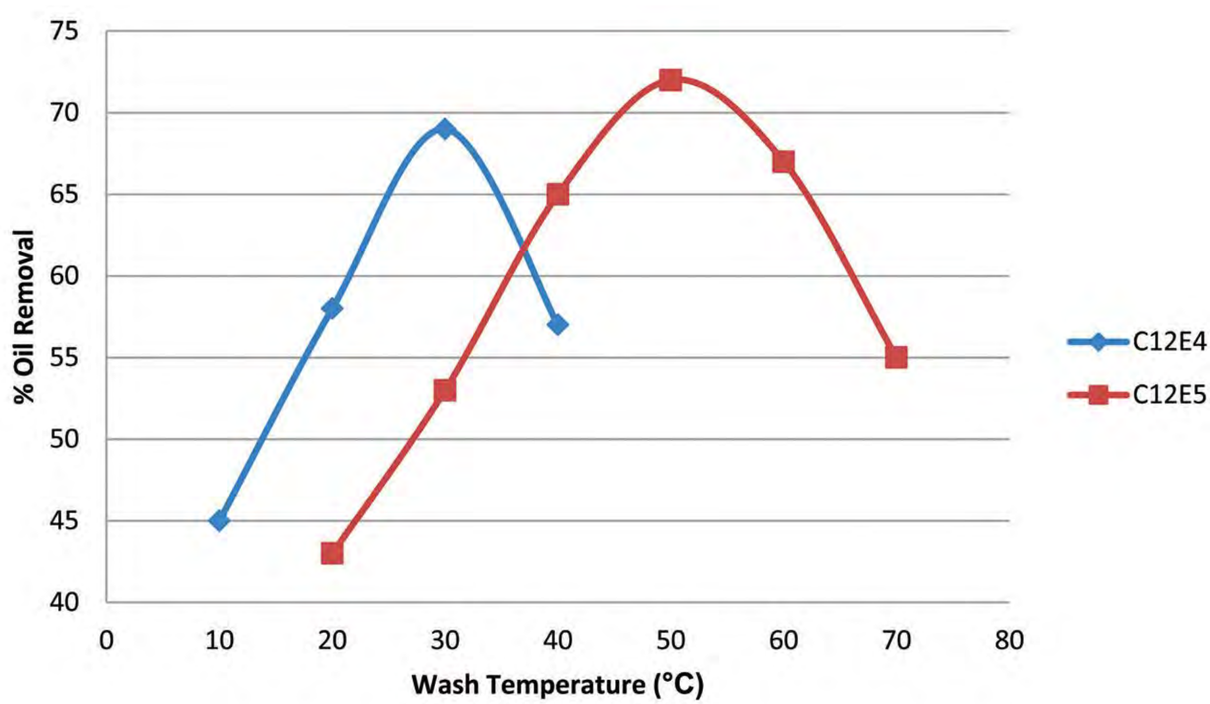

FIG. 3. Correlation of optimum nonpolar soil removal by specific alcohol ethoxylate surfactants from 65:35 polyester/cotton fabric with the oil-water-surfactant phase inversion temperature (PIT). Adapted from Miller and Raney (1993).

household laundering in the United States. In contrast to oil production, household laundering requires only a few grams of surfactant per washload, but billions of washloads are performed per year leading to the large overall surfactant consumption for this process.

MECHANISTIC COMPARISON

The removal of oil from a porous substrate by an aqueous medium can be related to the dimensionless capillary number, the ratio of viscous forces to the interfacial forces holding the oil in the pores:

$$N_c = \mu v/\gamma \qquad [1]$$

where N_c is capillary number, μ = viscosity of the flowing phase, v = velocity of flowing phase, and γ = interfacial tension between oil and water. As N_c increases, oil mobility increases. For chemical EOR, interfacial forces dominate as the flow rate through the rock is only about one foot (30 cm)/day. Therefore, ultralow interfacial tensions on the order of 10^{-3} dyne/cm are required to release significant quantities of the crude oil from the rock. Similarly, ultralow interfacial tensions are often present when oily soil detergency from fabric is optimized. However, the flow of washing solution through the fabric, as represented by v in Equation 1, also contributes significantly to efficient laundering, unlike in the chemical EOR process.

Surfactant systems for EOR are designed to provide the so-called Winsor III behavior, where surfactant solubility is balanced between oil and water, a middle-phase microemulsion is formed in a three-phase region, and oil-water interfacial tension is ultralow (see Fig. 2). For the anionic surfactants commonly used in EOR, this phase behavior occurs at the so-called optimum salinity for a given reservoir and temperature. In an analogous manner, optimum detergency of oily soils from synthetic fabrics using nonionic surfactants has been shown to occur at the phase inversion temperature (PIT), where phase and interfacial tension behavior identical to that found at optimum salinity is noted (Miller and Raney, 1993). Hence, surfactants for EOR and oily-soil detergency applications can be initially screened for effectiveness and optimized using the same indirect phase behavior and interfacial tension measurements.

Laboratory-scale performance screenings of surfactant systems for detergency and for EOR are similar in other ways. Washing soiled fabric swatches provides qualitative and/or quantitative measurements of detergency performance. Within Shell Chemicals R&D, radiotracer detergency techniques measuring oil levels in water have been used to identify and quantify optimized nonpolar oil removal at the PIT (see Fig. 3). For chemical EOR, separated efflu-

CONTINUED ON NEXT PAGE

FIG. 4. Sandstone core after alkaline surfactant polymer injection at left end (upper) and (lower) core cross sections showing residual oil after flooding (lower). Cross sections from top left to bottom right progress from inlet to outlet and show more residual oil near the outlet.

ents from core floods are typically used to quantify removal of crude oil from sandstone or carbonate cores. At the end of the core floods, the cores can be sectioned to qualitatively indicate the "cleanliness" of the rock after flooding with a controlled amount of surfactant solution. I have often noted that these qualitative observations of cross-sectioned rock samples, such as those in Figure 4, are very similar to observations of stained fabric swatches after laboratory detergency tests.

SURFACTANT REQUIREMENTS

The surfactants used in EOR and home laundering are generally different: Anionic surfactants for chemical EOR are typically high molecular weight anionic surfactants (e.g., having C_{20}–C_{24} hydrocarbon tails), whereas blends of anionic and nonionic surfactants with shorter, predominantly linear hydrophobes (e.g., C_{12}–C_{16}) are most commonly active ingredients in laundry detergents (Rosen and Kunjappu, 2012). In the last few years, branched anionic surfactants have gained favor for ASP processes due to their reduced tendency to form viscous liquid crystalline and microemulsion phases in the oil reservoir as compared to their linear analogs (Barnes *et al.*, 2008).

With regard to the formulations themselves, however, great similarities exist between the two applications. Typical formulations for a laundry powder and an ASP process are shown in Table 1. In addition to similar ingredients, it is quite interesting that the ratios of the three major ingredients are nearly the same—a 3:1 weight ratio of sodium carbonate to surfactant with a much lower level of polymer. Variations can occur, however, because chemical EOR is applied to reservoirs with wide differences in reservoir rock, crude oil, and formation water properties, the latter affecting the salinity of the water used in the formulation.

Despite their structural differences, surfactants for either application are prepared from the same feedstocks including olefins, alcohols, and alkylene oxides. As a result, direct competition for these feedstocks and the process units to make the surfactants will inevitably occur as full-scale ASP processes are initiated around the world and the volume of surfactants used for EOR approaches the amounts currently used for detergent applications.

PRODUCT FORMS

The shipment and storage of surfactant during commercial field operations is a huge problem for application of surfactant EOR. For a typical 100,000 bbl (16 million liters)/day injection, storage requirements for an offshore project to ensure uninterrupted supply

TABLE 1. Comparison of ingredients and dosage levels of a typical laundry detergent powder and alkaline-surfactant-polymer (ASP) enhanced oil recovery formulation

Ingredient	Example laundry powder	Typical ASP formulation
Surfactants	0.2 grams/liter	5 grams/liter
Soda ash	0.6 grams/liter	15 grams/liter
Polymer (acrylate-based)	0.01grams/liter (anti-redeposition–low MW)	1 gram/liter (viscosifying–high MW)
Other ingredients	Enzymes, fragrance, etc.	Co-solvent (optional for solubility enhancement)

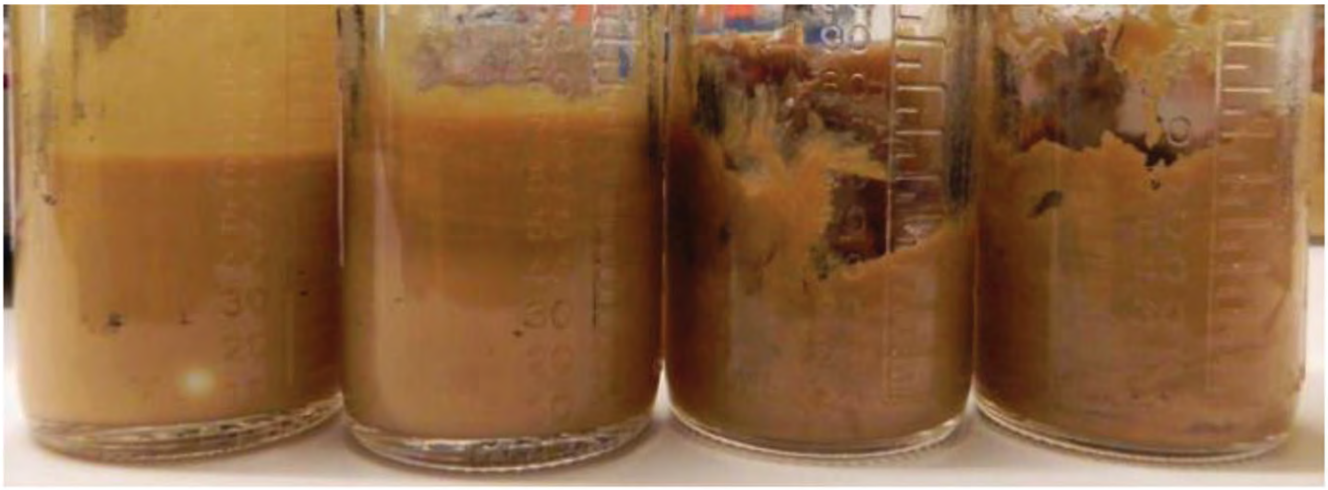

FIG. 5. Change in product consistency as water content is reduced from 80% to 30% (left to right) in an internal olefin sulfonate surfactant used for EOR.

of chemicals to the wells would be 7 million pounds (3,200 metric tons) of active surfactant and 17 million pounds (7,700 metric tons) of soda ash. Unfortunately, storage space is at a premium, particularly on deepwater production platforms, such as those found in the Gulf of Mexico (Raney *et al.*, 2012).

New concentrated surfactant forms would be useful to improve transportability and compactness of EOR surfactants. However, reducing water content from 70–80% to 20–30% for an EOR surfactant product typically converts the product form from a flowable liquid to very viscous pastes and gels (see Fig. 5). I believe technical advancements made by the laundry detergent industry, such as inclusion of small quantities of non-flammable solvents to produce flowable and easily dilutable compact heavy-duty laundry liquids, can be applied to this situation (Barnes *et al.*,2008). Similarly, technologies to produce compact laundry detergents containing sodium carbonate, surfactant, and polymer could be used to produce space-efficient powder forms for use in chemical EOR (Raney *et al.*, 2012; Barnes *et al.*, 2012). As already noted, the ratios of those three ingredients are quite similar for both powder laundry detergents and ASP EOR applications, making transfer of technologies fairly straightforward.

It is interesting to use Figure 5 to point out that two important surfactant characteristics for household detergent usage, color and odor, are of little consequence in EOR product forms.

ENVIRONMENTAL CONSIDERATIONS

Fresh water is a valuable resource around the world. In this regard, new low water-usage washing machines are important components of home laundering processes. In addition, past research between Shell and the Institute for Applied Surfactant Research (University of Oklahoma, Norman, USA) has

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For more information on EOR see *Inform 20*:682–685 (2009).

looked at the possibility of reusing both wash and rinse water for washing home laundry at an industrial scale (Scamehorn *et al.*, 2007). In initial studies, rinse and wash water were filtered through a 0.1 µm filter to remove oily and particulate soils and recirculated back to serve as a portion of the wash and rinse water for sequential washes in a home washing machine. Ninety percent water reuse and 40% surfactant recovery were achieved with little degradation in cleaning observed over the subsequent wash cycles.

Now, similar concepts are being used to allow reuse of water for chemical EOR. This process is specifically referred to as produced water reinjection (Raney *et al.*, 2012). Microfiltration of produced water removes the produced solids and residual oil droplets to a sufficient degree to allow reinjection of the water along with makeup chemicals without plugging the injection wells.

Fate of laundry detergent ingredients in municipal wastewater treatment facilities has been widely studied (Rosen and Kunjappu, 2012). Specific concerns about aquatic toxicity of surfactants and slow biodegradation of antiredeposition polymers are two key issues that have been mostly resolved by the detergent industry.

Produced water at offshore oil production facilities is commonly released into the ocean. Without additional expensive piping and pumps, produced water reinjection will not be an option in these situations, and the chemical EOR produced water will require not only removal of dispersed oil but also removal or degradation of produced surfactant and polymer (hundreds of parts per million) to allow its disposal into the ocean, that is, overboarding (Raney *et al.*, 2012). This need for environmentally benign water disposal is a major technology gap that must be addressed before widespread offshore chemical EOR can take place. What the detergent industry has learned regarding the aquatic fate and effects of surfactants and polymers will be quite helpful to understand the extent of treatment required for successful overboarding of offshore-produced water from chemical EOR processes.

Kirk H. Raney, a principal research engineer with Shell International Exploration and Production Inc,, USA, is a leading authority in laundry detergency technology and the underlying surfactant science. He may be contacted at +1 281-544-7810 or by email at kirk.raney@shell.com.

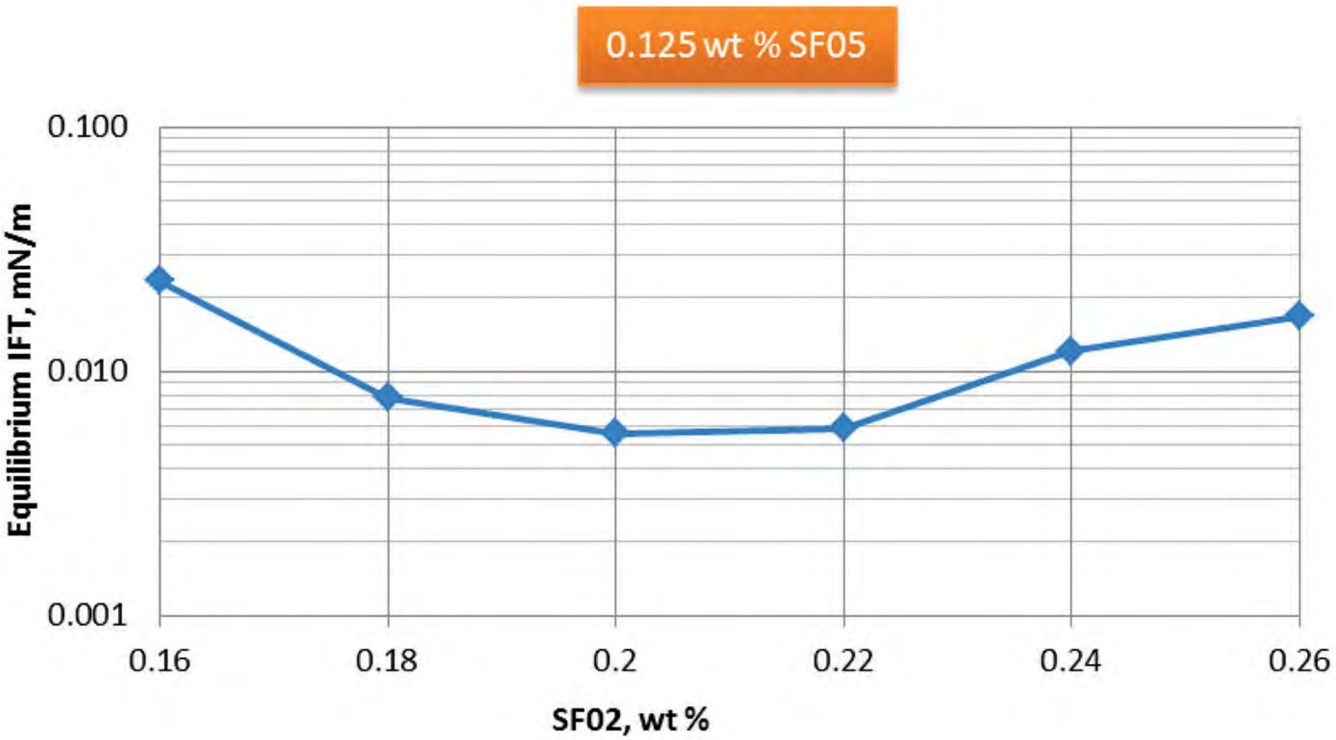

FIG. 1. Effect of SF02 concentration on IFT for a binary surfactant mixture (SF05/SF02). Abbreviations: where SF02, ethoxylated alcohol sulfate; SF05, propoxylated/ethoxylated alcohol sulfate ; IFT, interfacial tension.

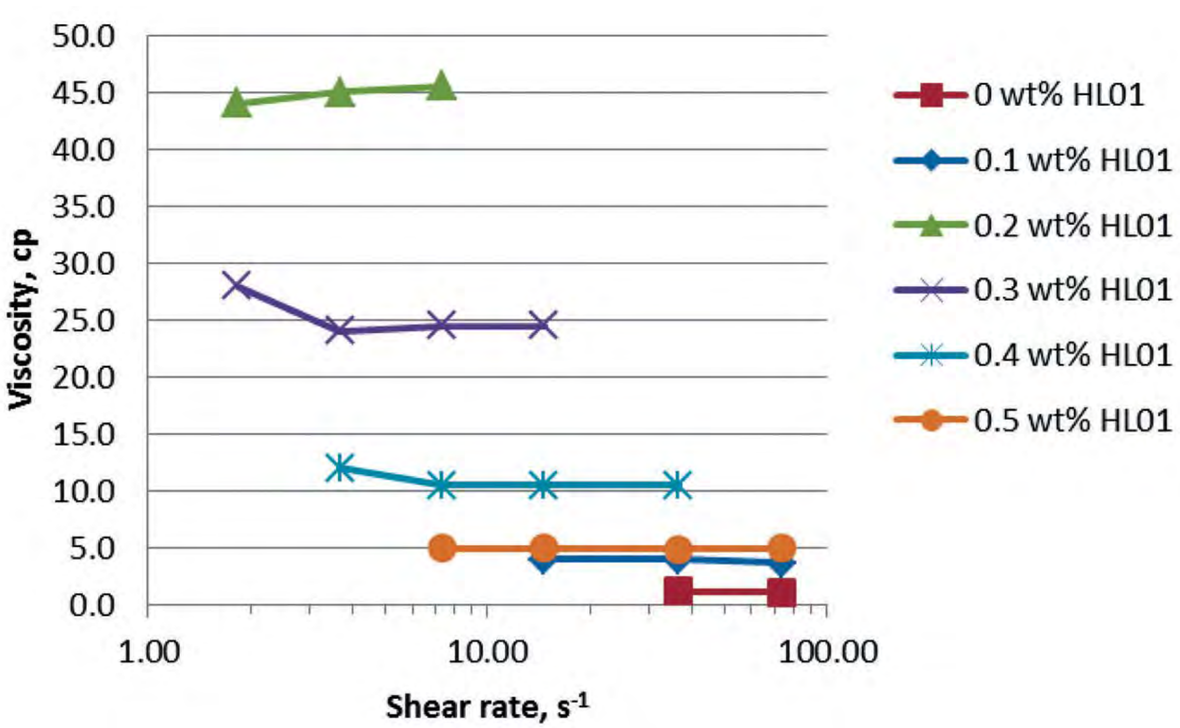

FIG. 2. Viscosity as a function of shear rate for wormlike micelles at different concentrations of hydrophilic linker (HL01) (a performance booster introduced for low IFT microemulsion system).

Designing surfactant-only formulations for a high salinity and tight reservoir

Wei Wan, Ajay Raj, Tzu-Ping Hsu, Prapas Lohateeraparp, Jeffrey H. Harwell, and Bor-Jier (Ben) Shiau

Increasing worldwide demand for fossil fuel due to strong economic growth in countries such as China and India partially explains the tight crude oil supply in the global market. Another contributing factor is that many existing oilfields are approaching their depletion stage, when the portion of recovered water (brine) is significantly greater than the amount of crude oil.

In a so-called high water-cut production well, for example, the oil and brine mixture that is produced may contain more than 95% water (brine), making oil recovery a technical challenge. Meanwhile, increasing demand for limited oil supplies has steadily contributed to an upward trend in crude oil prices. Consequently, researchers and industry alike are taking a serious look at technologies that can improve existing oil field production and efficiency rather than drilling new, deeper wells at unexplored offshore or onshore leases. In this article, we will briefly discuss some recent advances that have been made in designing surfactant formulations for field pilot testing of chemical flooding, or chemically enhanced oil recovery (CEOR).

SURFACTANT-ONLY FORMULATIONS FOR CHEMICAL CEOR

Among technologies for improving oil production, CEOR has been gaining a lot of attention based on some successful pilot tests done between 1970–1980 and more recent efforts as well (Awang *et al.*, 2012; Elraies *et al.*, 2010; Falls *et al.*, 1994). Most of these CEOR approaches involve a surfactant-only, polymer-only, surfactant-polymer, or alkaline-surfactant-polymer flood. Our main focus has been on exploring the injection of a surfactant-polymer system. More recently, we have turned our attention to designing a surfactant-only system for enhanced recovery in harsh conditions of high salinity (>150,000 ppm) and tighter rock formations (water permeability <25 millidarcy). Under such high levels of salinity, the injected anionic surfactants tend to fall out of solution due to precipitation or phase separation by the dissolved cations. In recent efforts, a binary surfactant mixture of propoxylated/ethoxylated alcohol sulfate and ethoxylated alcohol sulfate (with concentration of 0.325 wt%) demonstrated exceptional performance (with interfacial tension, IFT, of 0.006 mN/m) (Fig. 1). Our design approach uses site-specific produced water and a no-water treatment system for surfactant solution preparation. To streamline our surfactant-designing efforts, we have adapted the hydrophilic-lipophilic difference HLD) concept (to facilitate the surfactant screening tasks (as described in more detail in a separate document by Lohateeraparp *et al.*,2013).

Injecting a polymer solution combined with surfactant into tight sandstone formations creates additional technical challenges (e.g., excessive injection pressure, plugging the formation,

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- **As existing oilfields mature and approach depletion, their wells typically contain more water than crude oil, making oil recovery difficult. With the demand for fossil fuel increasing worldwide, researchers and industry are evaluating technologies that can improve production in such fields as an alternative to offshore drilling.**
- **Injecting mature wells with surfactants and other chemicals is one way to enhance oil recovery, but high-saline environments and tight reservoirs pose additional technical challenges.**
- **This article describes some of the specialized formulations that are being developed to address these technical challenges.**

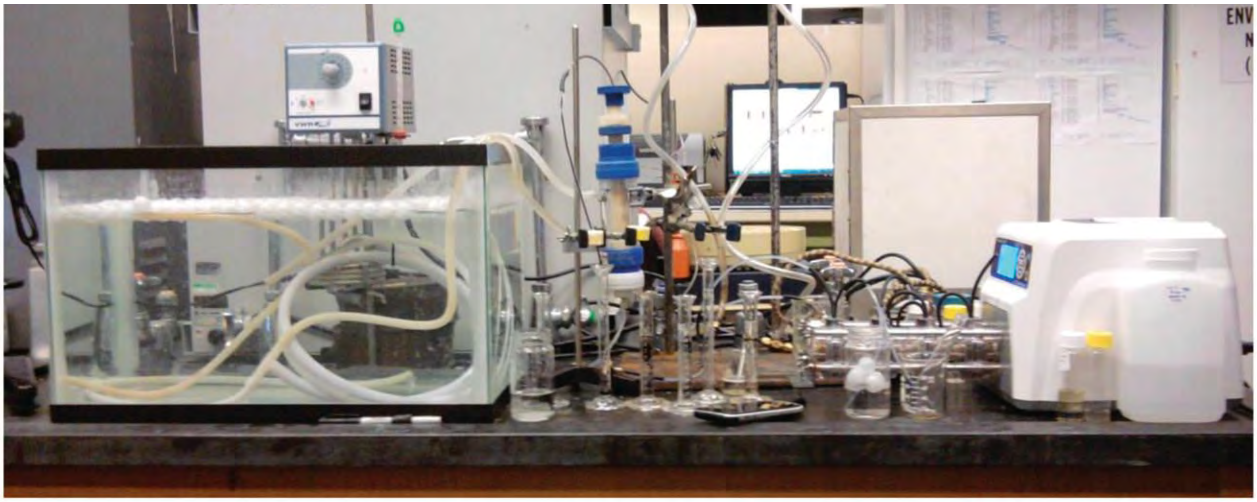

FIG. 3. Setup for one-dimensional sand-packed glass column tests (installed with blue end cap).

TABLE 1. Summary of oil recovery for different chemical flooding strategies with the selected binary surfactant system and pre-/post-chemical slug

Test #	Pre	Binary	Post	Oil recovery, %
1		1.5 PV		13
2	0.1 PV			8
3	0.5 PV			8
4		1.5 PV	0.5 PV	13
5	0.1 PV	1.5 PV	0.4 PV	25
6	0.1 PV	1.5 PV		25
7	0.1 PV	0.5 PV		17

[a]PV, pore volume.

or extreme slow recovery rate) for field implementation. To overcome these issues and enhance mobility control of the displaced oil bank (maintaining a plug flow of releasing oil) without plugging (or damaging) the formation rock, we explored the injection of a wormlike micelle solution. (Wormlike micelles are elongated aggregates of self-assembled surfactant molecules in aqueous solutions.) In one example, introducing wormlike micelles of anionic ethoxylated alcohol sulfate (1 wt%) combined with a hydrophilic linker (which increase the coalescence rate of microemulsions) produced the favorable viscosity of 45 cP at reservoir temperature of 36°C (Fig. 2, page 622). Further batch experiments indicated that the prepared surfactant and wormlike micelles solutions remained stable over an extended period in the batch reactor (>1 month).

The newly developed surfactant (a binary surfactant mixturee, injected typically between 0.2 to 1.5 pore volumes (PVs) of chemical slug size) and wormlike micelles (injected separately during pre- or post-chemical slug) formulations were further verified in one-dimensional sand-packed column with crushed Berea sandstone core to mimic the flow-through condition under reservoir temperature, while applying site-specific crude oil and brine to fine-tune the injection strategies and optimizing recovery performance for designing future field single-well pilot test (Fig. 3). Injection of 0.1 pore volume (PV) wormlike micelle system chasing with 1.5 PV surfactant-only slug achieved marked improvement of oil recovery (from 13% of recovery with no wormlike micelles to 25% recovery in the presence of wormlike additive) in the sand-packed column (Table 1).

DESIGNING PARAMETERS FOR WORMLIKE MICELLE SYSTEMS

Promising oil recovery data resulting from wormlike micelle additives led us to further explore various viscoelastic surfactant formulations with an eye toward creating a more favorable combined wormlike micelle/surfactant-only system for improving mobility control in tight formations without using conventional polymer injection approach. The rheological properties of wormlike micelles developed using different anionic surfactants were studied using natural and mimic brines under various reservoir conditions. It has been shown that key designing parameters such as the surfactant concentration, level of electrolytes, reservoir temperatures, and different co-surfactants have greater impact on the formation of wormlike micelles and their rheological properties (Berret, 2006; ;Safran *et al.*, 1990).

Our initial efforts are heavily focused on anionic ethoxylated alcohol sulfate to achieve wormlike micelles in natural and mimic brines (Fig. 4). For example, varying ethoxylation (EO) number changes the optimal salinity (NaCl) for maximum viscosity.

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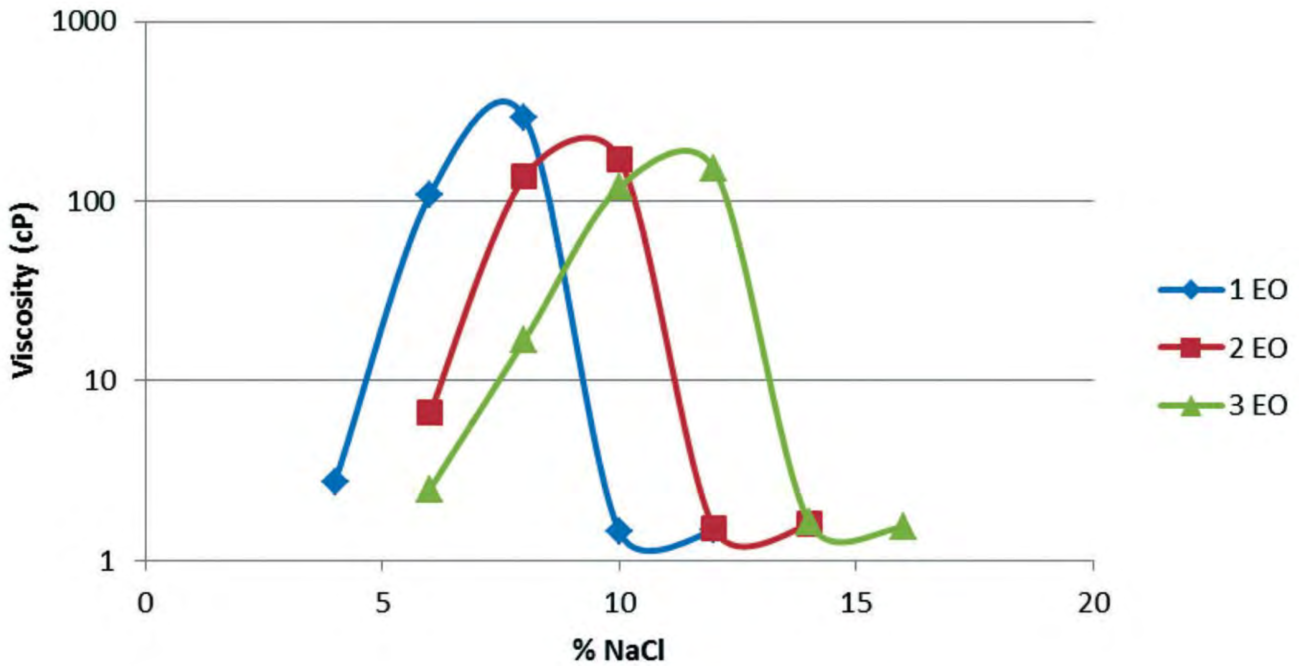

FIG. 4. Viscosity measurements obtained by varying the salt concentration of 1 wt% ethoxylated alcohol sulfate with different number of ethoxylation (EO) groups. Viscosity is measured at 25°C and a shear rate of 3.7 s^{-1}.

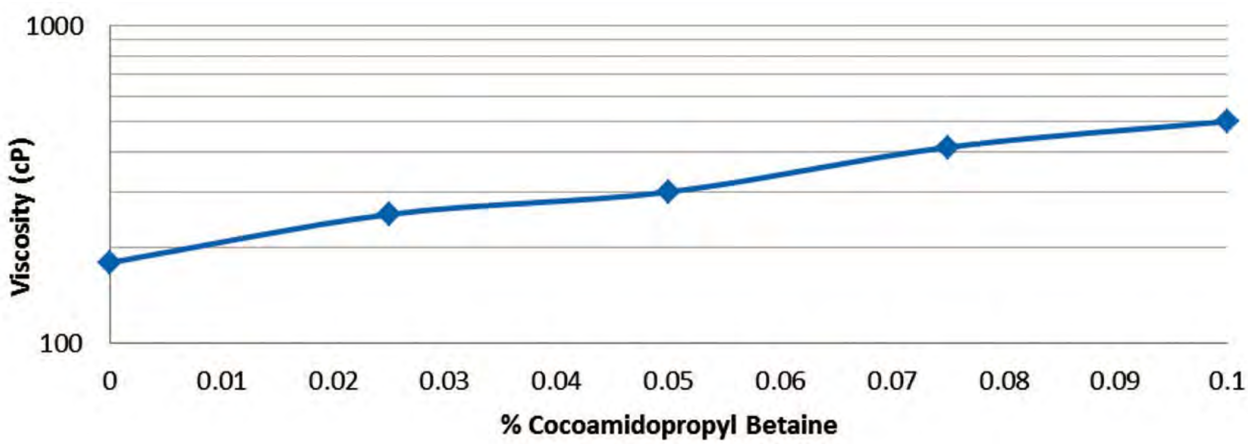

FIG. 5. Effect of betaine surfactant on wormlike micelle viscosity. Primary surfactant is 1 wt% ethoxylated alcohol sulfate with 3 ethoxylation number (EO) and the salt concentration is 10% NaCl. Viscosity is measured at 25°C and a shear rate of 3.7 s^{-1}.

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Oil production primer

Oil recovery occurs in three phases: primary, secondary, and tertiary. But because each reservoir has its own unique geologic and chemical makeup, the lines separating the three phases often are blurred.

Primary recovery occurs when internal pressure in a reservoir is high and oil all but spurts out of the ground. About 10% of available oil typically is removed in this phase. Secondary recovery, which can remove an additional 20-40% according to the US Department of Energy, consists of repressurizing the reservoir by pumping water or gases into it. The tertiary phase involves enhanced oil recovery (EOR) techniques that modify the reservoir system to allow the oil to flow more freely out of the well.

EOR techniques-which sometimes are also required in the primary and secondary phases of recovery-fall into three main categories: thermal, chemical, and solvent displacement. All of these involve the injection of fluids into the reservoir to generate fluid properties or interfacial conditions that are more favorable for oil displacement. The injection of steam heats the oil and makes it more fluid. Gas injection (generally natural gas, nitrogen, or carbon dioxide) pushes additional oil to a production well. Other gases that dissolve in the oil can be used, thereby thinning it and improving the flow rate.

Chemical EOR generally involves flooding a reservoir with an alkaline-surfactant-polymer combination, a surfactant-polymer mix, or a polymer-only injection. Current thinking suggests that the alkali reacts with acids and esters in the crude oil to form surfactants "that combine with the injected surfactant to produce synergistic mixtures at the oil/brine interface," according to Paul Berger and Christie Lee of Oil Chem Technologies, Inc., in Sugar Land, Texas, USA. "The alkali is also claimed to reduce the amount of surfactant adsorption onto the formation, especially in limestone reservoirs," they continue. Alkali however does have its drawbacks including the ability to form scale in the tubing as well as deep in the formation. This can result in decrease in injectivity and reduced or no flow into the pores containing oil. In addition, the surfactant reduces the interfacial tension and the polymer modifies viscosity, thereby increasing sweep efficiency.

Polymers used in EOR include polyacrylamide, AMPS (2-acrylamido-2-methyl propanesulfonic acid) copolymer, xanthan gum, and scleroglucan. To date, anionic surfactants have performed best in EOR. In general, highly branched hydrophobes are needed for low-viscosity micelles and microemulsions. Although ethylene has been the feedstock of choice in the past, Berger and Lee have found that naturally derived surfactants with a double bond serve equally well as branched petroleum-derived products. "Our patent US 7,556,098 illustrates this," Berger noted. Researchers are also looking at using genetically modified microorganisms that can produce biosurfactants *in situ*.

The decision about which surfactant to use depends on factors such as reservoir temperature, pressure, depth, salinity, and permeability. Each oilfield is different and has to be characterized before the most effective surfactant can be modeled and produced. The advent of high-throughput experimentation has allowed researchers to custom-make surfactants of high purity and specificity at relatively low cost.

Increase of ethoxylation number (i.e., 3 EO versus 1 EO) requires additional salt (increased from 4% to 6% NaCl) to form wormlike micelles. And the wormlike micelles of high (3) EO surfactant is also more salt tolerant than low (1) EO surfactant (i.e., marked decrease of viscosity at higher salinity of 13% NaCl for 3 EO case, Fig. 4, page 625). To increase the viscosity further without losing the solution stability, we may introduce co-surfactant additive for performance improvement.

The growth of wormlike micelles can also be positively initiated if co-surfactants or other low molecular weight additives are incorporated. Cocoamidopropyl betaine reportedly interacts with sodium dodecyl sulfate to form wormlike micelles and increases viscosity. Others have suggested that mixed cationic and anionic surfactants can produce strong electrostatic attractions between oppositely charged head groups, which lead to strong synergism and association in solution (Christov *et al*., 2004). By adding trace amounts of cocoamidopropyl betaine to ethoxylated alcohol sulfate, we can markedly increase the solution viscosity up to 500 cP without compromising the long-term stability of the surfactant solution (Fig. 5, page 625).

Our future efforts will expand on those newly developed viscoelastic surfactant formulations which are expected to offer better sweep efficiency (maintaining a plug-flow propagation of the released oil by injecting more viscous fluid than the target oil) in challenging tight formation and fewer limitations as compared to classical CEOR polymers for more permeable sandstone formations.

Wei Wan is a PhD student at Mewbourne School of Petroleum and Geological Engineering, University of Oklahoma (OU), Norman, USA. His educational backgrounds were in both energy and environmental engineering. His doctoral research is in areas of developing surfactant/polymer formulations for Chemical EOR, and field single-well tracer tests.

Ajay Raj is a recent MS graduate from School of Chemical, Biological, and Materials Engineering, OU. His thesis work involves developing surfactant-based viscoelastic formulations for mobility control in tight reservoirs.

Tzu-Ping Hsu is Laboratory Manager at Applied Surfactant Laboratory, OU. Mr. Hsu has over ten years of research experiences in formulations development and field implementation of surfactant flushing, most recently in chemical enhancing oil recovery. He holds MS degrees from Petroleum Engineering and Environmental Engineering.

Prapas Lohateeraparp is Operations Manager at Chemical Flooding Technologies, LLC, Tulsa, Oklahoma, USA. He has more than a dozen years of industry experiences involving laboratory feasibility studies, engineering designs and field testing on chemical flood for both EOR and environmental applications. He holds advanced degrees in Chemical Engineering and Petrochemical Technology.

Jeffrey Harwell is an AIChE fellow and the Asahi Glass Chair of Chemical Engineering at OU. His research focuses on the science and applications of surfactants, including especially the application of surfactants in environmental remediation. He is the author or co-author of over 140 refereed journal articles and coeditor of four books.

Ben Shiau is an associate professor of Petroleum Engineering and Director of Applied Surfactant Laboratory at OU. Dr. Shiau's research focuses on surfactant flooding, nanotechnologies for oil fields, and groundwater remediation systems. He is the author or co-author of over 20 refereed journal articles.

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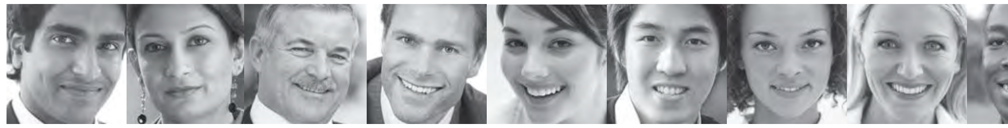

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Could panda gut microbes power the next-generation biorefinery?

Candace Williams,
Darrell Sparks, and Ashli Brown

Many factors hinder complete lignocellulose hydrolysis to simple sugars for use in biofuel production; this conversion requires that cellulose and hemicellulose be degraded into their respective monomers. A number of pretreatment methods have been tested to accomplish this. One possibility is biological treatment. Although enzymes produced by fungi, bacteria, and protozoans may require longer reaction times than other pretreatment methods, they are capable of breaking down the lignocellulosic materials.

THE POWER OF MICROBES

Cellulolytic organisms produce cellulases that are capable of degrading lignocellulosic biomass at body temperature, allowing for enzymatic hydrolysis of this biomass under mild conditions without the production of inhibiting by-products. Such characteristics make bacteria easily exploitable in the conversion of lignocellulosic biomass.

Cellulolytic anaerobes capable of hydrolyzing plant biomass have been isolated from many sources including landfill leachate, feces, mammalian gastrointestinal tracts, compost, soil, hot springs, and methanogenic sludge. An example of the ability of microorganisms found in fecal material to degrade biomass has been shown (Taguchi *et al.*, 2001) by combining kitchen refuse with bacterial strains isolated from the feces from giant pandas (*Ailuropoda melanoleuca*). A total of 24 kg of kitchen waste was reduced to less than 1 kg after four weeks, a digestion rate of 96%, indicating that microflora of the giant panda play a significant role in the reduction of biomass. Metagenomic analysis by Zhu and coworkers (2011) has confirmed the presence of a putative cellulose metabolism in the gut of the giant panda. Also, Williams and coworkers (2012) enumerated *Bacteroides* spp. and *Clostridium* spp. in the giant panda; they are of special interest due to their ability to produce cellulases capable of reducing lignocellulosic biomass.

INTEGRATING GIANT PANDA GUT MICROBES INTO A BIOFUELS PLATFORM

Most biofuels research focuses on either cellulose degradation or lipid production. What is unique about using giant panda gut microbes in a biofuels platform is that the microbial consortium would consist of not only cellulolytic organisms, which would be required to degrade lignocellulosic biomass into simple sugars, but also oleaginous organisms, which would accumulate lipids following consumption of simple sugars. Using feces from the Memphis Zoo's giant pandas, we have been able to use next-generation sequencing to parallelize sequencing of the giant panda gut microbiome, producing sequences for all microbes present concurrently.

Sequencing has identified 17 organisms from the giant panda's fecal microbiome with either cellulolytic or oleaginous properties that can be used in the production of lignocellulosic biomass-based biofuels. The presence of several organisms has been confirmed using polymerase chain reaction (PCR) with species-specific primers, but validation is still in progress (Table 1).

These cellulolytic organisms can be used to pretreat lignocellulosic biomass, converting the biomass into simple sugars that can be used by oleaginous microbes to accumulate lipids. The consumption of simple sugars by oleaginous organisms would inhibit negative feedback of cellulolytic organisms that might otherwise reduce cellulase production in the presence of high concentrations of simple sugars. This would allow for more accumulation of lipids that can then be converted into renewable diesel and biodiesel.

With such a complex consortium, which involves integrating cellulose degradation and lipid production, finding optimal conditions for all microbes has not been easy. In our preliminary study (Williams, *et al.* 2013), organisms degraded cellobiose (a cellulose surrogate) and accumulated transesterifiable lipids under anaerobic conditions. Microbial degradation of cellulose to sugar was determined by using high-performance liquid chromatography–evaporative light-scattering detection to quantify sugar production, indicating that time and cellobiose concentration effects were significant with respect to sugar consumption (time, $P = 0.0015$; concentration, $P < 0.0001$) and that 65.4% of cellobiose was consumed over five days. Lipid accumulation was monitored by performing Bligh-Dyer (chloroform/methanol/water) lipid extraction of lyophilized cells. Total lipid extracts and individual fatty acid production were tracked using fatty acid methyl ester (FAME) analysis with gas chromatography-flame ionization detection. Transesterifiable lipid accumulation was observed.

FUTURE GOALS

Preliminary analyses have shown the ability of the giant panda's microbes to convert lignocellulosic biomass into lipids for use in an oil-based biofuels platform. However, there is still much to be done. Once optimal conditions are determined, the next step is to further characterize the consortium. A baseline for the giant panda gut microbiome already has been created by sequencing microbial DNA from feces from both pandas housed at the Memphis Zoo

CONTINUED ON NEXT PAGE

- **Next-generation sequencing has verified the presence of cellulolytic and oleaginous microbes in the gut microbiome of the giant panda.**
- **These organisms display the ability to reduce a cellulose surrogate and accumulate lipids.**
- **Integration of panda gut microbes into a biofuels platform may help reduce costs associated with producing second-generation biofuels.**

TABLE 1. Organisms identified using next-generation sequencing, their function, and validation

Organism	Function[a]	Validation
Acetivibrio cellulolyticus	C/O	–
Bacteroides fragilis	C	–
Burkholderia pseudomallei	C	–
Clostridium cellulolyticum	C	–
Clostridium cellulovorans	C	+
Clostridium lentocellum	C	–
Clostridium novyi	C	–
Clostridium phytofermentans	C	–
Clostridium thermocellum	C/O	–
Fibrobacter succinogenes	C	–
Pseudomonas fluorescens	O	+
Pseudomonas putida	O	+
Ruminococcus albus	C	–
Saccharophagus degradans	C/O	+
Shewanella piezotolerans	C/O	+
Sorangium cellulosum	C/O	–
Streptococcus gallolyticus	C	+
Thermanaerobacterium thermosaccharolyticum	C	+

[a]C, cellulolytic; O, oleaginous.

[FAST FACT: Doggie doo power?]

Welsh company Streetkleen has developed a way of turning dog waste into methane to provide renewable energy. The method uses anaerobic digestion to produce methane from dog wastes accumulated in dog waste collection tanks. The methane can then be sent directly to an appliance, such as a streetlamp, heater, or the like, to provide renewable energy for its operation.

Streetkleen's first unit, which was set to begin operation in July 2013 and can take up to three metric tonnes of waste a day, powers a turbine that generates up to 200,000 kilowatt hours of electricity per year, which can power up to 60 homes. The company hopes to lead a commercial-scale venture to divert 700,000 metric tons of dog waste generated annually in Britain to methane production, saving £70 million ($105 million or €81,700,000) in landfill charges and fees.

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and their bamboo via Roche's 454 pyrosequencing platform. The figure of the platform can be viewed in this issue's supplement (digital and mobile editions only). This method is a next-generation sequencing technology that relies on the "sequencing by synthesis" principle, which involves the detection of pyrophosphate release upon the incorporation of nucleotides to determine sequence. Pyrosequencing allowed us to determine that organisms sequenced are residents of the gut and not transients. Principal coordinate analysis indicates that these organisms are residents of the gut, and not microbes brought in on bamboo. Further 454 pyrosequencing will be done to measure change in abundance of the consortium's microorganisms over time, which will allow us to home in on which organisms are playing key roles in cellulose degradation and lipid accumulation. The activity of the enzyme systems and processes associated with these metabolic pathways will also be evaluated.

Another future aim is to look for eukaryotes that may be present in the panda gut microbiome. Cellulolytic fungi are known to exist in other herbivores such as cattle and sheep, but they have yet to be identified in the giant panda. These organisms may play an integral role in the digestion of lignocellulosic biomass and accumulation of lipids. Roche's 454 pyrosequencing platform will also be used to determine presence and abundance of these organisms.

Preliminary results from the integration of organisms that reside in the gut of the giant panda into a biofuels platform have shown promise, as reflected by their ability to reduce a cellulose surrogate and accumulate lipids. The use of this unique herbivorous carnivore's gut microbes could help to reduce the costs of producing second-generation lignocellulosic-based biofuels, thus creating a usable product from two waste materials.

Candace Williams is a Ph.D. student in the department of biochemistry, molecular biology, entomology and plant pathology at Mississippi State University (MSU), USA, currently studying the symbiosis of the giant panda and the red panda with their respective gastrointestinal microfloras. Her background is microbiology, and her current research areas include conservation and biofuels. She can be reached at clw224@msstate.edu.

Darrell Sparks is an assistant professor in the department of biochemistry, molecular biology, entomology, and plant pathology at MSU and serves as director of chemical regulatory services at the Mississippi State Chemical Laboratory. Prior to joining the faculty at MSU, Sparks was director of extraction technologies with the Renewable Fuels and Chemicals Laboratory, School of Engineering, MSU. His background is in biochemical engineering, and his current areas of research include biofuels, conservation, environmental remediation, and mitigation of food/feed contaminants.

Ashli Brown is an assistant professor in the department of biochemistry, molecular biology, entomology, and plant pathology at MSU and serves as director of research and the pesticide residue group at the Mississippi State Chemical Laboratory. Much of her research is focused on the optimization of renewable alternatives such as green fuel, biodiesel, and bioethanol (including the use of panda gut microflora to generate biofuels). To improve food safety, she is also identifying and characterizing factors in Aspergillus *that control the degradation of aflatoxin.*

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Thanakorn Vegetable Oil Products Co. Ltd.
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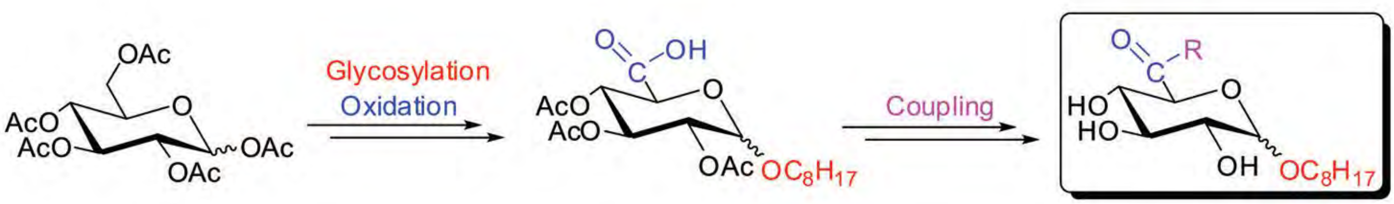
Seven new biobased surfactant technologies

GLUCOSE-BASED SURFACTANT WITH CALCIUM CHELATING PROPERTIES FOR HARD-WATER DETERGENCY

01



Feedstock
Glucose, fatty alcohol, amino acids

Synthetic process
Glycosylation, oxidation, coupling

Charge
Nonionic and anionic surfactants

Yield
48% to 88% from the octyl-D-glucopyranosiduronic acid

Solubility
Not determined, higher than the critical micelle concentration (CMC)

Biodegradability
Expected

- Biobased surfactants continue to gain market share owing to concerns about sustainability and the long-term availability of petrochemical feedstocks.
- New technologies are making it easier than ever to make such products from renewable feedstocks. Technically, everything that can be made from petroleum-based feedstocks can now be made from biomaterials, with the dream of going 100% bio being limited only by nontechnical factors such as price, reliability of supply, and labeling.
- Here are seven novel biobased surfactant technologies worth noting.

Interfacial properties/ surface tension measurements
γ_{CMC} : 32–45 mN m^{-1} (pH of the solution without acid or base additives)

CMC characteristics
19–32 mmol L^{-1}

Krafft temperature
Not determined

Foaming properties
Medium to good

Chelating ability
Ca^{2+}, Fe^{3+}

Potential applications
1. Detergency: some surfactants retain foaming properties even in calcium solutions.
2. Fe^{3+} removal from water phases by a flotation process.

Benefits
1. These surfactants are able to foam even in calcium solutions without any usual detergent additives.
2. Possible selective removal of Fe^{3+} from water phases by the flotation process.

Drawbacks
Price.

Citations

Ferlin, N., D. Grassi, C. Ojeda, M.J.L. Castro, A. Fernández-Cirelli, J. Kovensky, and E. Grand, Calcium chelating sugar-based surfactants for hard-water detergency, *J. Surfact. Deterg. 15*:259–264, 2012

Ferlin, N., D. Grassi, C. Ojeda, M.J.L. Castro, E. Grand, A. Fernández-Cirelli, and J. Kovensky, Synthesis of sugar-based chelating surfactants for metal removal from wastewater, *Carbohydr. Res. 343*:839–847, 2008

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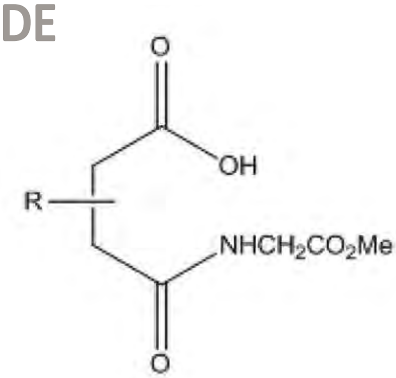
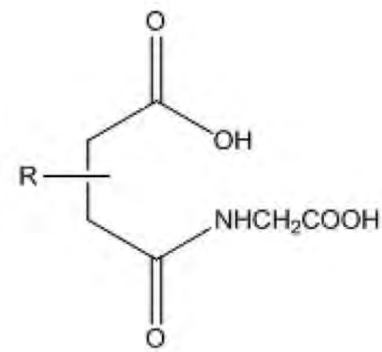
02

AMINO ACID SOAPS DERIVED FROM DODECENYL SUCCINIC ANHYDRIDE





Feedstock
The dodecenyl succinic anhydride is obtained from petroleum feedstocks. There is potential to make *n*-alkyl succinic anhydrides from plant oils. The surfactant is formed by reaction with the methyl ester of glycine to give a monocarboxylate surfactant. The ester can then be hydrolyzed to yield a dicarboxylic acid.

Synthetic process
Amide formation and hydrolysis

Yield
85%

Solubility
Water-soluble at 20°C, but limit not measured

Biodegradability
Not known

Interfacial properties/ surface tension measurements
For the monocarboxylate, 28 mN m^{-1} at pH 7, 40.5 mN m^{-1} at pH 10. For the dicarboxylate, 28.7 mN m^{-1} at pH 7 and 36.4 mN m^{-1} at pH 10.

CMC characteristics
For the monocarboxylate, ~2 mmol dm^{-3} at pH7, 8.3 mmol dm^{-3} at pH 10. For the dicarboxylate. ~1 mmol dm^{-3} at pH 7 and 100 mmol dm^{-3} at pH 10

Krafft temperature
Below 20°C, but not measured

Foaming properties
Not measured

Chelating ability
The dicarboxylate surfactant shows a low surface tension (~28 mN m^{-1} at pH 7) in the presence of ~1 mmol dm^{-3} of calcium ions at a 1:1 surfactant/calcium ion ratio.

Potential applications
For chelating divalent metal ions

Benefits
A biorenewable material (glycine) is used to make the head group

Drawbacks
Petroleum-based hydrocarbon chain

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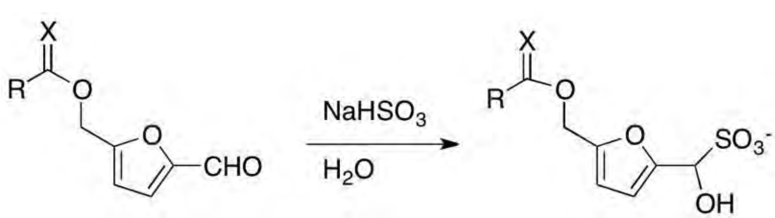
03

FURAN METHANE SULFONATES



Feedstock
Glucose/fructose

Synthetic process
Acid-catalyzed conversion of carbohydrate into furan followed by addition of bisulfite to carbonyl group

Charge
Sodium salt of a sulfonic acid

Yield
60%–98%

Solubility
Good in MeOH

Biodegradability
Should be easily biodegradable

Krafft temperature
Ranges: 77–82° C

Benefits
Mild source of SO$_3^-$, product precipitates from solution as white solid

Drawbacks
Limited stability in base

Citation
Kraus, G.A., and J.J. Lee, A direct synthesis of renewable sulfonate-based surfactants, *J. Surfact. Deterg.* *16*:317–320, 2013

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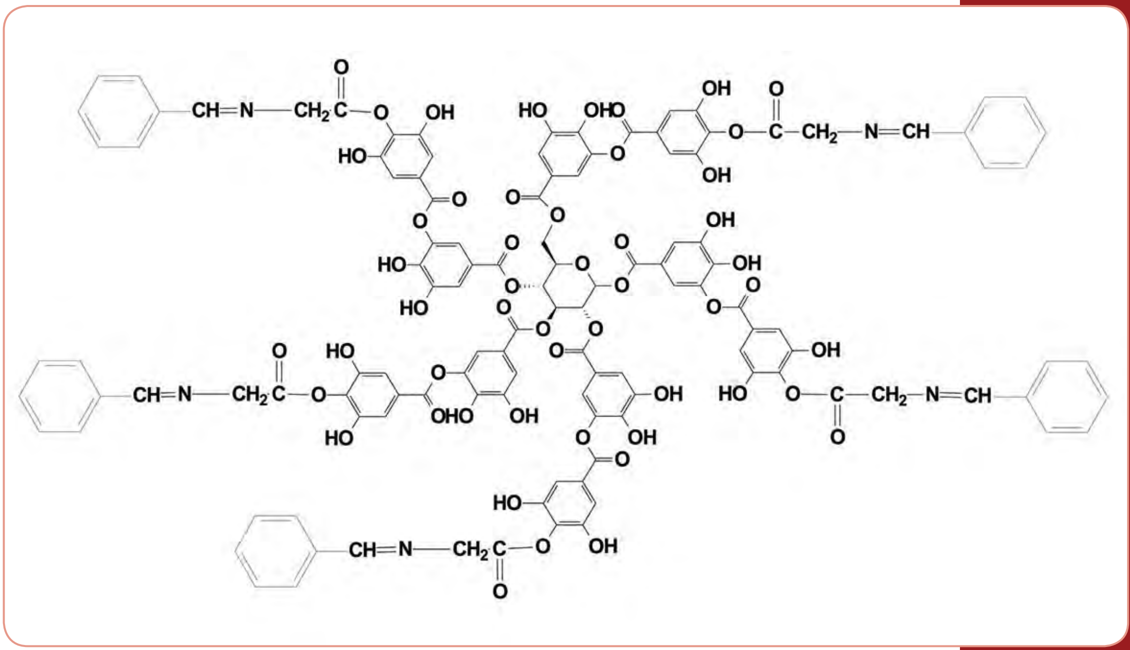
04

TANNIC ACID–FATTY ACID NONIONIC SURFACTANTS



Feedstock
Tannic acid, glycine, benzaldehyde, and fatty acids

Synthetic process
Esterification

Yield
About 85% based on the reactants

Solubility
Completely soluble in water and partially soluble in organic solvents preferably toluene and xylene

Biodegradability
Meets European specifications defining biodegradability (100–85% after 28 days in fresh water)

Interfacial properties/ surface tension measurements
35–45 mN m^{-1} at pH = 7

CMC characteristics
0.18–0.65 mM L^{-1} at 25°C

Krafft temperature
Over 85°C, depending on the type of fatty acids

Foaming properties
Low-foaming

Chelating ability
Forms metal complexes with transition metals and preferably with Cu, Co, Pb, Hg, and Fe

Potential applications
Biocides

Benefits
In petroleum and domestic applications

Drawbacks
Degrades in a high pH medium (pH over 11)

Citation
Negm, N.A., A.F. El Farargy, I.A. Mohammad, M.F. Zaki, and M.M. Khowdiary, Synthesis and inhibitory activity of Schiff base surfactants derived from tannic acid and their cobalt (III), manganese (II) and iron (III) complexes against bacteria and fungi, *J. Surfact. Deterg. 16*:767–777, 2013

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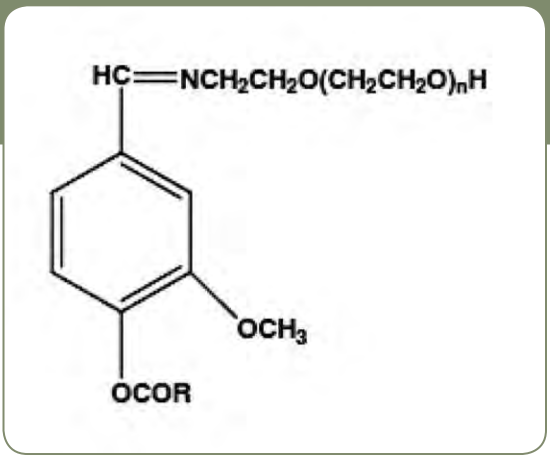
VANILLIN-NONIONIC SURFACTANT

05



Feedstock
Vanillin, ethanolamine, fatty acid

Synthetic process
Esterification

Yield
About 90% with respect to the reactants

Solubility
Completely soluble in water and partially soluble in organic solvents preferably toluene and xylene

Biodegradability
Meets European specifications defining biodegradabil-

ity (100–85% after 28 days in fresh water)

Interfacial properties/ surface tension measurements
32–42 mN m^{-1} at pH =7

CMC characteristics
0.1825–1.48 mM L^{-1} at 25°C

Krafft temperature
Over 57–85°C depending on the type of fatty acids

Foaming properties
Low-foaming

Chelating ability
Form metal complexes with transition metals, preferably Cu, Co, Pb, Hg, and Fe

Potential applications
Biocides

Benefits
In drilling applications

Drawbacks
Cannot resist a high-pH medium (>11)

Citation
Sayed, G.H., F.M. Ghuiba, M.I. Abdou, E.A.A. Badr, S.M. Tawfik, and N.A.M. Negm, Synthesis, surface, thermodynamic properties of some biodegradable vanillin-modified polyoxyethylene surfactants, *J. Surfact. Deterg. 15*:735–743, 2012

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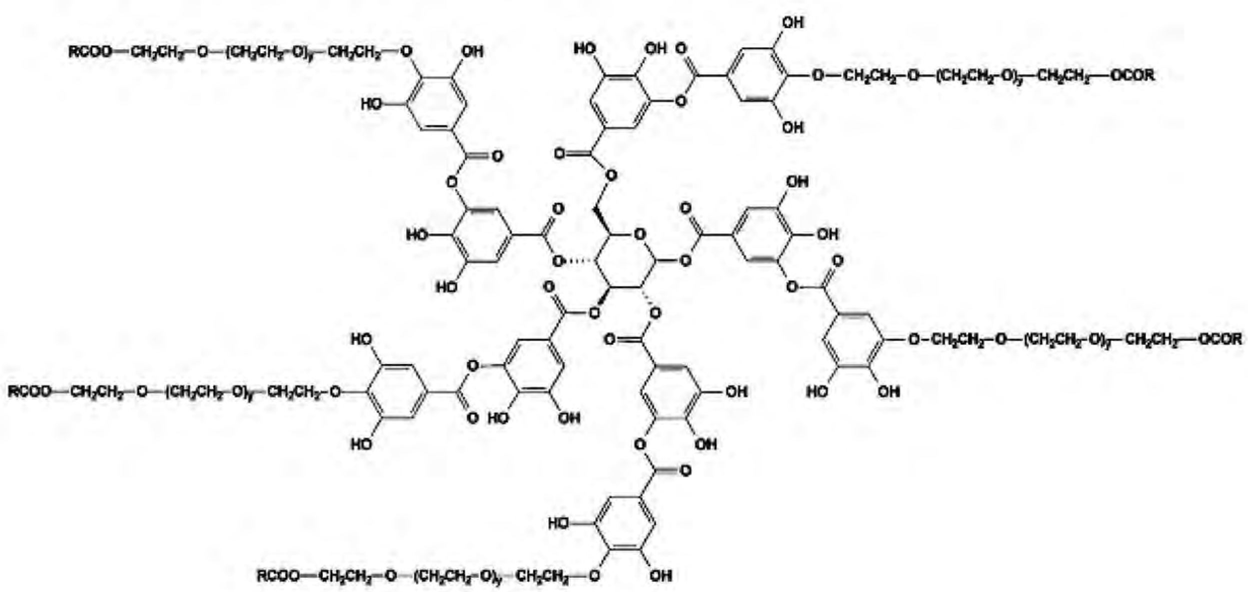
06 TANNIC ACID–POLYETHYLENE GLYCOL NONIONIC SURFACTANTS



Feedstocks
Tannic acid, polyethylene glycols (molecular weight: 400, 600, 1000, and 2000 g mol^{-1}), and fatty acids

Synthetic process
Esterification

Yield
About 85% based on the reactants

Solubility
Completely soluble in water and partially soluble in organic solvents preferably toluene and xylene

Biodegradability
Agree by the European specifications (75% after 28 days in fresh water)

Interfacial properties/ surface tension measurements
3.–40 mN m^{-1} at pH = 7

CMC characteristics
0.2–1.2 mM L^{-1} at 25°C

Krafft temperature
Over 92°C depending on the polyethylene glycol molecular weight

Foaming properties
Low-foaming

CONTINUED ON NEXT PAGE

Chelating ability
Forms metal complexes with transition metals and preferably Cu, Co, Pb, Hg, and Fe

Potential applications
Corrosion inhibitors, emulsifiers, and wetting agents

Benefits
In petroleum, tissue, coating applications

Drawbacks
Cannot resist a high pH medium (>11)

Citation
Negm, N.A., A.F.M. El Farargy, D.E. Mohammed, and H.N. Mohamad, Environmentally friendly nonionic surfactants derived from tannic acid: synthesis, characterization and surface activity, *J. Surfact. Deterg. 15*:433–443, 2012.

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A FLEXIBLE PROCESS MODEL TO ESTIMATE THE ECONOMICS OF LARGE-SCALE SOPHOROLIPID BIOSYNTHESIS VIA FERMENTATION 07

NOTE: This technology is not itself a biosurfactant. It is an economic model that can be used to assess the economic feasibility of biosurfactants known as sophorolipids.

Summary
This study developed a process economic model for the fermentative synthesis of sophorolipids using contemporary process simulation software and current reagent, equipment, and supply costs, following current production practices. Glucose and either high-oleic sunflower oil or oleic acid were used as feedstocks, and the annual production capacity of the plant was set at 90.7 million kilograms per year with continuous operation of 24 hours a day for 330 days per year. Major equipment costs and other considerations such as capital, labor, material and utilities costs were included in the model.

The single greatest contributor to the overall production/operating cost was determined to be raw materials, which accounted for 89% and 87% of the total estimated production expenditures for the high-oleic sunflower oil and oleic acid-based fermentations, respectively. Based on this model and yields of 100 g L^{-1}, the cost of large-scale sophorolipid synthesis via fermentation from glucose/high-oleic sunflower oil was calculated to be US$2.95/kg ($1.34/lb) and from glucose/oleic acid to be US$2.54/kg ($1.15/lb).

Feedstock

Sophorolipids can be produced from both triacylglycerol and free fatty acid substrates. Because of this and the preference for 17-hydroxyoleic acid as the hydrophobic moiety in the sophorolipid molecules, two different lipidic carbon sources (high-oleic sunflower oil and oleic acid) were modeled for comparison. In both cases glucose was used as the carbohydrate source.

Synthetic process

Certain yeast species (primarily from the genus Candida) produce sophorolipids when they are grown under favorable conditions. Therefore, the model was based on a fed-batch fermentation protocol that we had developed in our laboratory using whole-cell catalysis and assuming yields of 100 grams of sophorolipids per liter of fermentation medium.

Potential applications

This model will be applied to determine the production costs of sophorolipids compared to other more common petroleum-based surfactants in order to assess the economic feasibility of using sophorolipids in place of or as an additive in industries where surfactants are commonly employed or in niche markets where no comparable alternative currently exists.

Benefits

The major benefit of the model is flexibility. One can introduce new steps or methods into the model, and the economic effects of those alterations can be determined thus helping to optimize production and isolation parameters. In addition, the model can draw attention to the most costly operations, thus helping the design engineer to focus on the areas where cost-reduction may be possible.

Citations

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Production of value-added co-products in industrial oilseeds

Kristi D. Snell and Oliver P. Peoples

Levels of carbon dioxide in the world's atmosphere continue to rise and recently reached levels that haven't been observed since prehistoric times (Biello, 2013). The main cause of these increases is considered to be the burning of fossil fuels (Le Quéré *et al.*, 2013). Given the scale and cost structure achievable through agriculture, it is not surprising that interest in producing fuels, chemicals, and materials from plants has increased to address not only global warming but also concerns regarding fossil fuel feedstock availability. Use of plants instead of fossil fuels as feedstocks in the chemical and energy sectors can help address both issues by providing the dual benefits of renewable carbon substrates with consumption of carbon dioxide from plant photosynthesis.

Establishing a profitable renewable fuels business that can compete with the petroleum industry, which produces multiple products from one crude feedstock, is challenging. Applying a co-product strategy to energy crops that is similar to that currently used in the petroleum industry can add additional revenue streams and increase profit margins for biorefineries, making them more sustainable businesses (Snell and Peoples, 2009).

- **Engineered co-products in industrial oilseeds provide additional revenue streams—beyond biodiesel—that are essential to make biorefineries profitable.**
- **The biopolymer polyhydroxybutyrate (PHB) is an ideal co-product for oilseeds with applications in the nutrition and industrial markets.**

FIG. 1. (Upper panel) Plot of camelina from a Metabolix field trial containing plants with immature seed pods. The tip of a yardstick is visible in the center of the plot. (Lower left panel) Mature seed pods before harvest. (Lower right panel) Mature seeds and opened seed pods.

Camelina sativa (Fig. 1) is an oilseed crop that can benefit from genetic modifications to allow accumulation of co-products that increase the crop's value and will be used here as an illustration that can be applied to other oilseeds. Camelina has been receiving considerable attention as a crop for the production of liquid biofuels owing to its high seed oil content, its ability to grow on marginal land with minimal inputs, and its limited food use. Detailed descriptions of camelina and of its benefits as an energy crop have appeared in three separate articles in the November/December 2011 issue of *Inform*.

While acreage devoted to camelina growth is currently low, the US Environmental Protection Agency recently qualified biofuels produced from camelina oil as biomass-based diesels or advanced biofuels allowing them to participate in fulfilling Renewable Fuel Standard (RFS) quotas for blending of biofuels into traditional fossil fuels (http://tinyurl.com/EPA-RFS-Feb-13). This ruling should provide more stable market opportunities for camelina oil. The crop will still, however, require additional value-added revenue streams from processing to provide a stable business.

The typical processing of conventional camelina yields oil, which can be converted to liquid fuels, and meal, which can be used as a supplement in animal feed or burned as a solid fuel (Fig. 2, top, page 642). Camelina meal contains a high protein content and its use as a feed additive has been approved by the US Food and Drug Administration at levels of up to 10% in feeds for beef cattle, broiler chickens, and laying hens; and swine at levels of up to 2% (Eynck *et al.*, 2013).

Scientists at Metabolix and Metabolix Oilseeds, a wholly owned subsidiary of Metabolix located in Saskatoon, Canada, have been working to engineer the production of the biopolymer polyhydroxybutyrate (PHB) into the seeds of camelina such that the engineered seed could be processed to produce additional value-added co-products (Fig. 2, bottom, page 642). PHB is the simplest member of the versatile family of polyhydroxyalkanoate (PHA) polymers that naturally accumulate in some bacteria as a carbon and energy reserve in the presence of excess amounts of a carbon-rich substrate, much like animals accumulate fat. The bacteria can later mobilize the stored carbon to provide energy for growth. PHB is an ideal co-product for energy crops such as camelina since it can be accumulated in seeds as discrete granules of sequestered carbon by engineering bacterial genes encoding the biochemical pathway for polymer formation into the plant. The host plant is not able to access the carbon once it is polymerized, allowing the potential accumulation of high levels of the material. Metabolix has generated lines that produce polymer at commercial levels, and further work to translate these results into field-ready lines is under way.

PHB is a unique biological molecule in that it has applications in multiple markets, including plastics, chemicals, and enhanced feeds. All of these markets are potentially large-volume markets that are scalable with the energy sector.

• The size of these markets is scalable with the energy sector, a necessary feature for a co-product in an energy crop.

PHB IN PLASTICS

Industrial interest in PHAs has focused on their use as biodegradable plastics with properties that make them suitable replacements for

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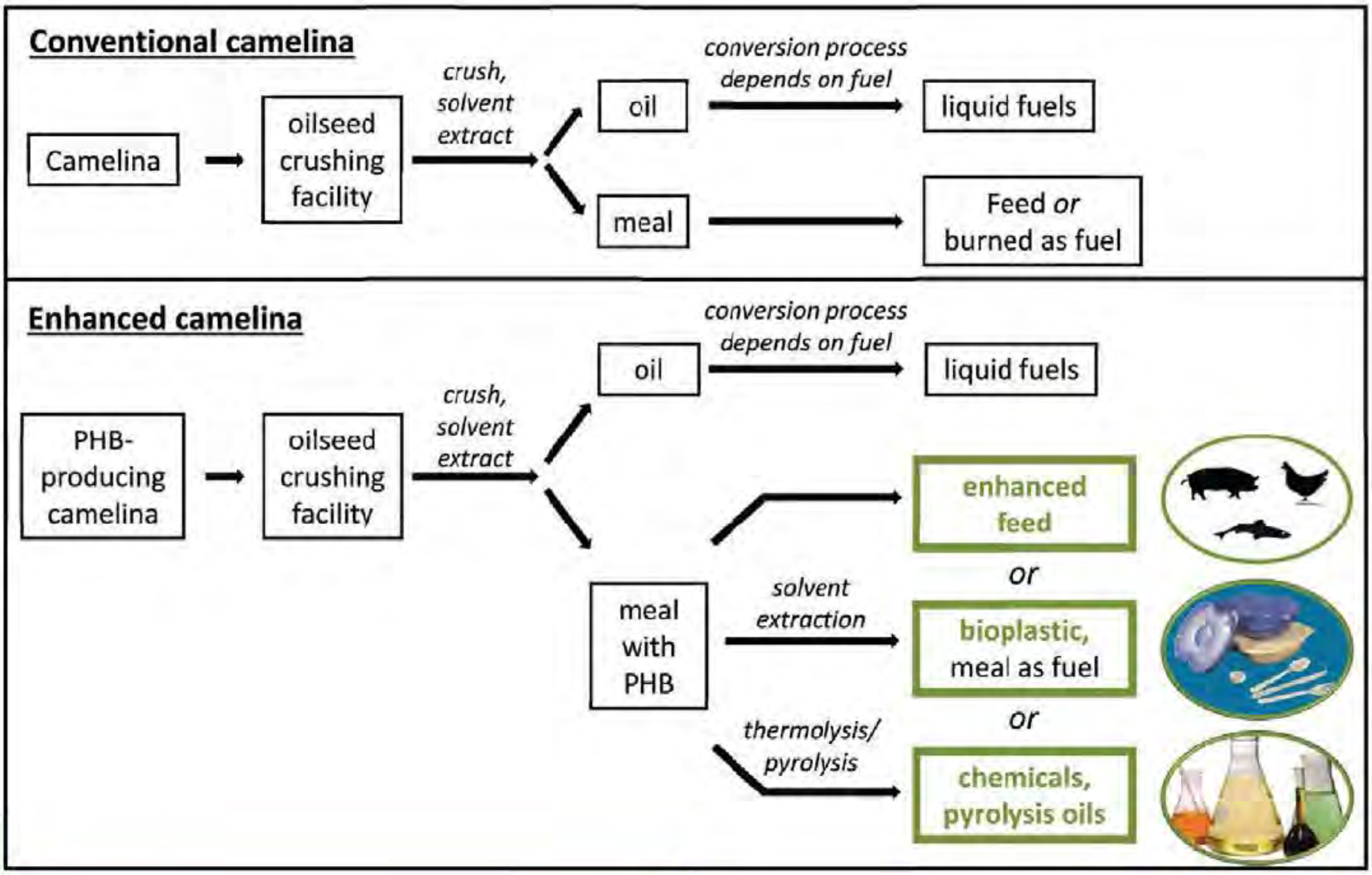

FIG. 2. Polyhydroxybutyrate (PHB)-containing camelina increases the value of the seed, and its meal can be used to produce enhanced feeds, bioplastics, or chemicals. Meal to be used as an enhanced feed can be generated in a conventional oilseed crushing facility while bioplastics and chemicals will require additional capital equipment for production. Products that enhance the value of the crop are shown in green.

many petroleum-derived plastics. The monomer unit composition of the polymer dictates its properties, which can range from elastomeric and soft to brittle. Although the plastics properties of the homopolymer PHB are more limited than other PHAs, we envision plant-based production to provide a cheap source of polymeric material whose properties can be improved with blending and additives. The properties of polylactic acid, a leading renewable bioplastic whose monomer unit is produced by microbial fermentation, are improved in a similar fashion with blends and additives.

PHB IN ENHANCED FEEDS

PHB can also be used as a supplement to generate enhanced feeds. Multiple studies have shown that PHB added to animal feed can provide increased feed conversion values, protection from pathogenic bacteria, and/or prebiotic effects (Somleva *et al.*, 2013), especially in aquaculture. Feed is a particularly

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exciting opportunity for PHB-producing camelina since the high protein content of the PHB-containing meal after oil removal can be used directly to produce enhanced value-added feeds with no capital costs beyond what is required in a typical oilseed crushing facility. In fish feed, this meal can be a partial substitution for the fish meal component of feeds that are currently fed to carnivorous fish. Supply of fish meal and fish oil to the aquaculture industry contributes to the overfishing of oceans (Naylor *et al.*, 200_), and reductions in the use of these components in feed would increase the industry's sustainability.

PHB AS FEEDSTOCK FOR CHEMICALS

In another application for PHAs, researchers at Metabolix have developed technology to convert the polymers to chemicals using a simple heating process (FAST™ process). This allows the polymer backbone to break, producing in the case of PHB crotonic acid, a molecule that can be chemically converted to commodity products such as *n*-butanol, an advanced biofuel, or propylene, a precursor to polypropylene. Other researchers have already made efforts to produce pyrolysis liquids from conventional camelina meal that yielded high-quality, high-energy liquid fuel intermediates (Boateng *et al.*, 2010). Use of PHB camelina meal in a similar process could provide an additional revenue stream from the production of crotonic acid.

The multiple markets and market flexibility of PHB enhance its value as a target molecule for energy crops that can be used to provide a greater return on the significant investment needed to develop the crop and biorefinery technology. Products that can be obtained from PHB-containing camelina seeds can significantly increase the value of the crop, providing profitability for the farmer and increased return on investment for the biorefinery business that processes the crop. While PHB-producing camelina has been used as an illustration, engineering of other oilseeds would provide similar economic opportunities.

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Ultrasound in palm oil milling: a paradigm shift for a traditional process

This year's AOCS Corporate Achievement Award went to Ladang Tai Tak Sdn. Bhd. (Malaysia) and partners CSIRO (Australia) and IHMS Sdn. Bhd. (Malaysia). The following article describes their award-winning work.

- **Ultrasound technology has potential to significantly increase oil recovery and reduce waste streams in the milling of palm oil.**
- **The technology is economically affordable and has been proven in a semi-commercial 5 metric ton (fresh fruit bunches per hour) plant; full-scale commercial operation is being planned.**
- **The benefits of ultrasound application in industrial plants—including increased yield of oil from fresh fruit bunches, enhanced throughput, and reduced waste solids and energy consumption—are being quantified.**

Mary Ann Augustin, Keong Hoe Lee, and Phil Clarke

The major vegetable oil produced in the world is palm oil, and it is the most consumed edible oil. Palm oil is extracted from the mesocarp of the palm fruit. Most palm oil mills handle between 60 and 120 metric tons (MT) of fresh fruit bunches (FFB) per hour using a traditional palm oil milling process to extract the oil from the fruit.

The traditional process begins with the sterilization of the FFB, followed by stripping of the palm fruits, which

are then reheated and mashed in a digester, and pressed using a continuous screw press. The hot (85–90°C) liquor exiting from the screw press (ex-screw press feed which is comprised of oil mixed with residual vegetal material and foreign matter) is then fed into a vertical clarification tank (VCT). The oil is allowed to separate under gravity, a process which usually takes 1–3 hours. The hot oil is drawn off from the top, clarified, and dewatered. The lower sludge fraction (sludge underflow), which contains some entrapped oil, is centrifuged to recover additional oil and returned to the VCT for further separation by gravity settling. The remaining post-centrifugation sludge (palm oil mill effluent, or POME) is a waste stream.

OIL LOSS IN PALM OIL MILLS AND POME: AN OPPORTUNITY FOR IMPROVEMENT

The oil recovery from palm oil milling operations depends on many factors such as ripeness of the fruits and losses throughout the various unit processes. Oil may be lost in the sterilizer condensate, in the form of fruit remaining in incompletely stripped fruit bunches, sludge, and POME. The POME is an environmental pollutant as it contains biodegradable organic material and thus must be processed before release. The oil loss in the POME is usually greater than 0.5% oil on a FFB basis or 2.50% on an oil basis.

Any intervention that improves the recovery of palm oil during milling and lessens the oil lost in POME would potentially produce both commercial and environmental benefits..

The opportunity for improving the palm oil milling process was realized by bringing together the expert knowledge of the palm oil milling operations and sound science underpinning ultrasonic technology application to emulsion systems. A patent covering the use of ultrasound for enhanced oil recovery has been filed (Augustin *et al.*, 2012).

CAPITALIZING ON THE USE OF HIGH-FREQUENCY ULTRASOUND

With ultrasound technology, acoustic pressure waves are applied to a material to assist in the processing operation. The frequencies of the acoustic waves usually range from ~18–100 kHz (low frequency) to 500–3,000 kHz (high frequency). In the food industry, low frequency ultrasound has generally been used to assist in extraction of components from plant material, an effect that has been attributed to the disruption of cell walls. Low frequency has also been used for emulsification of oils. On the other hand, high frequency ultrasound (megasonics) may be used to enhance separation of oil. Acoustic separation by high frequency ultrasound occurs in the presence of standing waves, where oil particles move to the antinodes as soil and vegetal material migrate to the nodes. This facilitates the separation of oil from non-oil solids and the de-emulsification of oil.

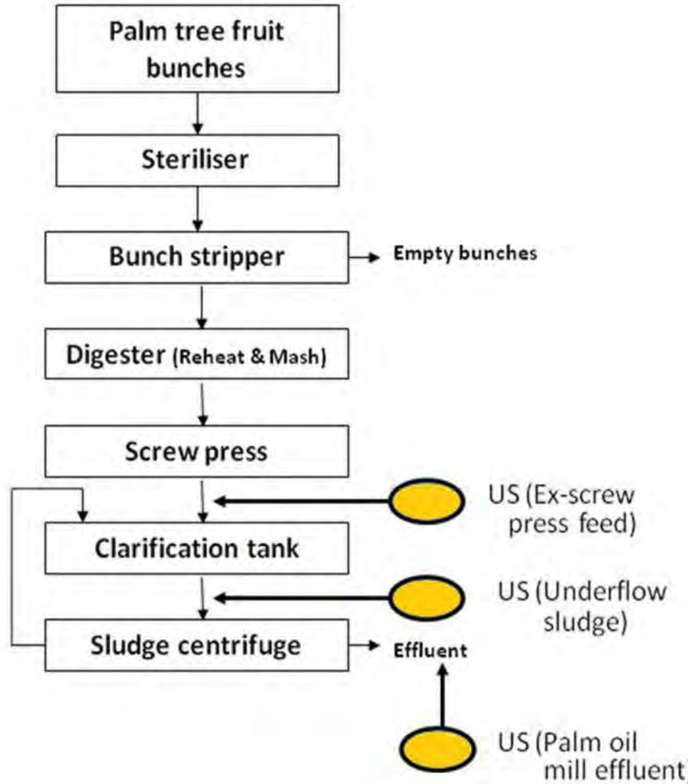

FIG. 1. Potential points of application of ultrasound (US) in the palm oil milling process.

Ultrasound can potentially be applied at many points in the palm oil milling process (Fig. 1). Initial trials were carried out in a laboratory on (i) the ex-screw press feed, (ii) the underflow sludge from the clarifier tank, and (iii) the POME. From these initial determinations of oil recovery efficiency resulting from the application of ultrasound, the ex-screw press feed was chosen as the desired point of intervention for practical application.

With the potential of high frequency ultrasound for improving oil recovery having been proven on a laboratory scale (Juliano *et al.*, 2013a), further trials were carried out on a pilot scale in 100-liter vessels using a batch process (Fig. 2, page 646). These trials demonstrated that high frequency ultrasound speeds up the gravity separation of the oil, reduces the amount of oil in the sludge underflow from the clarification process, and improves oil recovery overall. The enhanced oil recovery did not affect the

CONTINUED ON NEXT PAGE

FIG. 2. Pilot-scale trials in matched 100-liter vessels showing increased amounts of decantable oil on application of ultrasound.

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quality of the oil, as demonstrated by the similar DOBI (deterioration of bleachability index) values, vitamin E content, and free fatty acid values for oil obtained with or without the application of ultrasound (Juliano *et al.*, 2103b).

The application of high frequency ultrasound was then designed to be carried out as a continuous process in a palm oil mill. The ultrasound-assisted separation and enhanced recovery of palm oil in milling operations have been successfully scaled up and trialled in a continuous 5 MT (FFB) per hour plant (Ladang Tai Tak Sdn. Bhd., Johor, Malaysia). In these validation trials, an average 1.40 kg extra oil/MT palm fruit bunch was recovered with ultrasound intervention. This increased oil recovery was for a well-run palm oil milling operation.

Full-scale commercial operation is being planned. This will allow the benefits of the process to be mapped and quantified.

IMPACT AND POTENTIAL BENEFITS

If one estimates that the application of ultrasound technology recovers an extra 0.1 to 0.2% of oil from the FFB, then a mill producing an average 200–400 MT of oil per annum could provide an extra US$200,000 to US$400,000 each year. By using these estimates of oil recoveries and the cost of ultrasound transducers and associated equipment for this application from an equipment supplier, the recovery costs for implementation of this technology would be approximately two years, if only the oil recovery is taken into account.

Other benefits may accrue with the use of the ultrasound technology in palm oil milling. For example, a new palm oil mill plant could benefit from the faster free oil separation in the clarification tank, thereby providing the potential for higher throughputs in addition to a smaller equipment (clarifier) footprint and lower energy requirements for clarification. Increased recovery of oil from the ex-screw press feed, leading to reduced oil in POME, reduces the biological oxygen demand of the effluents, providing flow-on environmental benefits.

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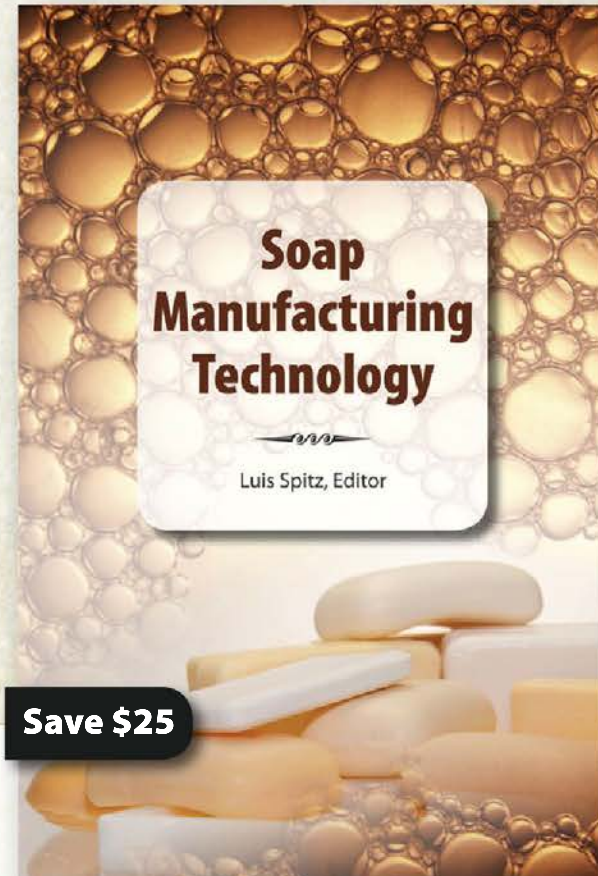

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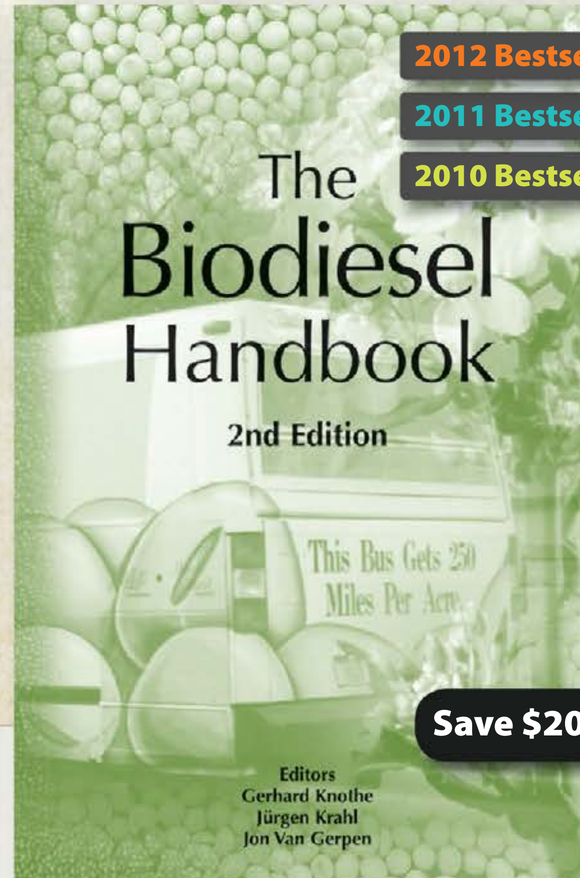

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Luis Spitz, Editor

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Engineered oilseed crops with fish oil DHA levels

James R. Petrie, Peter D. Nichols, Malcolm Devine, and Surinder P. Singh

- **Developing an oilseed source of omega-3 long-chain (≥C20) polyunsaturated fatty acids (ω3 LC-PUFA, termed long-chain ω3 here) is desirable, as these long-chain ω3 provide far stronger health benefits than the shorter-chain plant precursors of these fatty acids, α-linolenic acid (ALA, 18:3ω3) and stearidonic acid (SDA, 18:4ω3) (Turchini *et al.*, 2012).**

- **Consequently, engineering marine oils into land plants has been a long-standing goal of oilseed bioengineers. However, since both the long- and shorter-chain fatty acids are commonly referred to as "omega-3," it is difficult for consumers to recognize the difference.**

- **This article provides a progress update for the most challenging long-chain ω3 fatty acid docosahexaenoic acid (DHA).**

The aquaculture industry has been the main user of fish oil for several decades. Owing to increasing costs, and with fish oil being a finite resource, it is now often substituted with vegetable oils. But the limited conversion of ALA to eicosapentaenoic acid (EPA) and DHA in fish hampers the use of vegetable oils in aquafeeds, with the result that long-chain ω3 content in farmed seafood is decreasing. It was hypothesized that using SDA-containing oils could overcome the rate-limiting step in converting ALA to long-chain ω3 (Miller *et al.*, 2008), and indeed Atlantic salmon parr maintained long-chain ω3 content when supplemented with *Echium* oil containing SDA. However, little conversion of SDA to EPA and in particular DHA occurred in Atlantic salmon smolt (the larger seawater phase) (Miller *et al.*, 2008). The same observations occurred for trials with the iconic marine teleost fish barramundi with virtually no long-chain ω3, particularly DHA, being produced or accumulated in this species.

A crucial question is: How effectively is the shorter-chain ALA, already found in some plant oils, metabolized to DHA in humans? A review of human and animal studies (Brenna *et al.*, 2009) stated that ALA bioconversion to long-chain ω3 has been observed in nearly all humans irrespective of gender and from infants up to middle age. However, the authors concluded that current evidence indicates that the conversion of ALA to DHA is of the order of 1% in infants, but considerably lower (almost nil) in adults. They observed that supplementation with preformed EPA results in around 15-fold more efficient conversion to DHA than ALA supplementation. Unsurprisingly, they also observed that supplementation with preformed DHA is the most efficient way to increase DHA concentration in blood and tissues. The authors observed as well that bioconversion of ALA into long-chain ω3 was reduced by dietary linoleic acid (LA), a common ω3 fatty acid in plant oils; and there is strong evidence that LA intake negatively influences tissue concentrations of long-chain ω3.

The ω3 index (the combined total of erythrocyte membrane EPA and DHA as a percentage of total lipids) has emerged as a novel biomarker that predicts cardiovascular risk (Harris and von Schacky, 2004). Since there is typically no increase in DHA following SDA feeding in humans (Harris *et al.*, 2008), the reported beneficial rise in the ω3 index has been driven by an increase in EPA. In view of the overall cardiovascular benefits specific to DHA, including the anti-arrhythmic actions, further research is needed to assess whether an ω3 index that increased solely due to EPA is of less benefit than a rise in ω3 index achieved via greater incorporation of DHA into erythrocytes.

TABLE 1. Megatons (Mt) of ω3 long-chain polyunsaturated fatty acids(long-chain ω3) required if the global population was to meet specified recommended daily intakes (RDI)[a]

Specified RDI, or Current Intake[b]	EPA+DHA RDI (mg/day)	Global requirement (Mt/year)
WHO/EU	250	0.65
Mortality study[c]	400	1.02
Australia (National Heart Foundation)	500	1.28
Japan	1000	2.55
FAO/WHO Expert Consultation	250–2000[d]	0.65–5.1
USA (American Heart Association):		
Coronary heart disease sufferers	1000	2.55
Those seeking to reduce blood fats	2000–4000	5.1–10.2

[a]Current oceanic production of long-chain ω3 is 0.53 Mt/year.
[b]Nichols, P.D., J.R. Petrie, and P. Singh, Long-chain omega-3 oils—an update on sustainable sources, *Nutrients 2*:572–585 (2010).
[c]Mozaffarian, D., R.N. Lemaitre, I.B. King, X. Song, H. Huang, *et al.*, Plasma phospholipid long-chain ω-3 fatty acids and total and cause-specific mortality in older adults: a cohort study, *Ann. Int. Med. 158*:515–525 (2013).
[d]For secondary prevention of coronary heart disease. Abbreviations: EPA, eicosapentaenoic acid; DHA, docosahexaenoic acid: WHO, World Health Organization; EU, European Union; FAO, United Nations Food and Agriculture Organization.

SUPPLY AND DEMAND FOR LONG-CHAIN ω3

Demand for long-chain ω3 is primarily generated by two uses: aquaculture feed and human consumption, either by eating fish directly or by consuming long-chain ω3 in supplements and fortified foods such as eggs, baking products, and milk. More recently, use of more purified forms of long-chain ω3 in the pharmaceutical industry has also been growing. Importantly, the primary producers of long-chain ω3 are not fish but rather marine algae, with the long-chain ω3 being concentrated through the food chain in krill and small fish. Fish production in aquaculture does reduce pressure on ocean fish stocks, but aquaculture species still require an independent source of long-chain ω3. The current primary source of these long-chain ω3 oils for aquaculture is fish meal and fish oil from the ocean harvest with the most important species being coldwater fish such as Pacific anchovy, and to a lesser extent other oily fish including menhaden, cod, salmon, and tuna.

Peruvian anchovy stocks are closely monitored, and the annual harvest is strictly managed to maintain sufficient populations of breeding fish. As demand for long-chain ω3 increases, therefore, alternative sources are required. Two potential new sources are direct harvest from algae and higher plants. Since marine microalgae are the primary source of long-chain ω3, algal culture would appear to be a logical alternative source. To date, however, algal production systems have been limited by high capital costs and limited production, though time will tell if sufficient improvements can lead to higher and more economic levels of production.

As aquaculture becomes a more important source of fish for global human consumption, additional sources of long-chain ω3 oils are required to maintain desirable DHA levels in the farmed fish. Given the importance of these fatty acids in maintaining human health, an assured supply of high-quality long-chain ω3 is a high priority. Recommendations of daily intake (RDI) range from 250 to over 1,000 mg EPA + DHA/day. Table 1 describes the demand generated by the extrapolation of these RDI across the global population. The current oceanic supply clearly cannot meet the demand required for maintaining optimal human health combined with the needs of the aquaculture industry. Other sources that are more sustainable in the long term are required.

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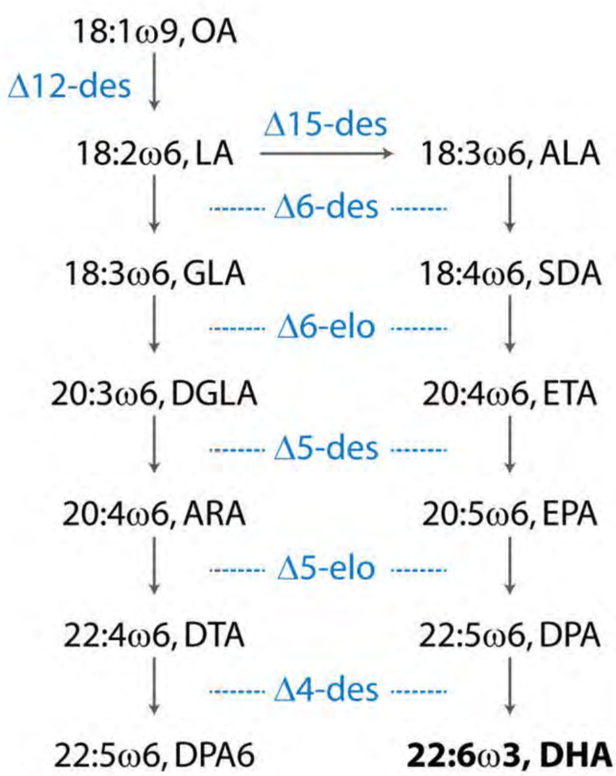

FIG. 1. The Δ6-desaturase ω3 long-chain polyunsaturated fatty acid synthesis pathway. This is the pathway used to engineer DHA oilseeds described in this article. Native OA, LA, and ALA are converted to DHA by transgenic enzymes. Abbreviations: OA, oleic acid; LA, linoleic acid; ALA, alpha linolenic acid; GLA, gamma linolenic acid; SDA, stearidonic acid; DGLA, dihomo-gamma linolenic acid; ETA, eicosatrienoic acid; ARA, arachidonic acid; EPA, eicosapentaenoic acid; DTA, docosatetraenoic acid; DPA, docosapentaenoic acid; DHA, docosahexaenoic acid; elo, elongase; des, desaturase.

ENGINEERING PLANT SEED DHA

Although higher plants can be a significant source of shorter-chain (C18) PUFA, they are not a source of long-chain ω3 such as EPA and DHA. The ability to produce industrially relevant levels of DHA in oilseed crops has been a long-standing target of the global lipid engineering community. The earliest proof-of-concept demonstrations were described in 2,005 scientific articles and patents (Nichols *et al.*, 2010; and references therein) with three groups describing the production of low levels of DHA in *Arabidopsis thaliana* (a laboratory model plant), *Brassica juncea*, and soybean. Multiple synthesis routes were explored in seed during the early years of DHA engineering exploration. These included the typical aerobic Δ6-desaturase pathway as shown in Figure 1, a parallel aerobic Δ9-elongase pathway, and an anaerobic polyketide synthase pathway. However, much of the effort following the initial proof-of-concept studies focused on EPA, a simpler engineering target than DHA, which took several years to develop.

The next significant breakthrough in DHA levels was reported by CSIRO in 2012 (Petrie *et al.*, 2012; and references therein). The authors described the production of fish oil-like levels of DHA (in excess of 12%) in Arabidopsis seed by the transgenic introduction of a single, multigene construct containing a novel Δ6-desaturase pathway. CSIRO identified an optimal gene combination using a rapid leaf-based assay to screen numerous candidate enzymes. They were also able to quickly optimize the function of their multigene construct designs using a similar system. In addition to the DHA yield, the fatty acid profile was also remarkably "clean" with very low levels of ω6 fatty acids and ω3 intermediate fatty acids produced by the transgenic pathway. In addition, consumer surveys showed high acceptance across Australia and the United States for potential future products, with a preference indicated for use in feeds.

The authors can now report similar results in an oilseed crop, *Camelina sativa*. The CSIRO/Nuseed/Grains Research

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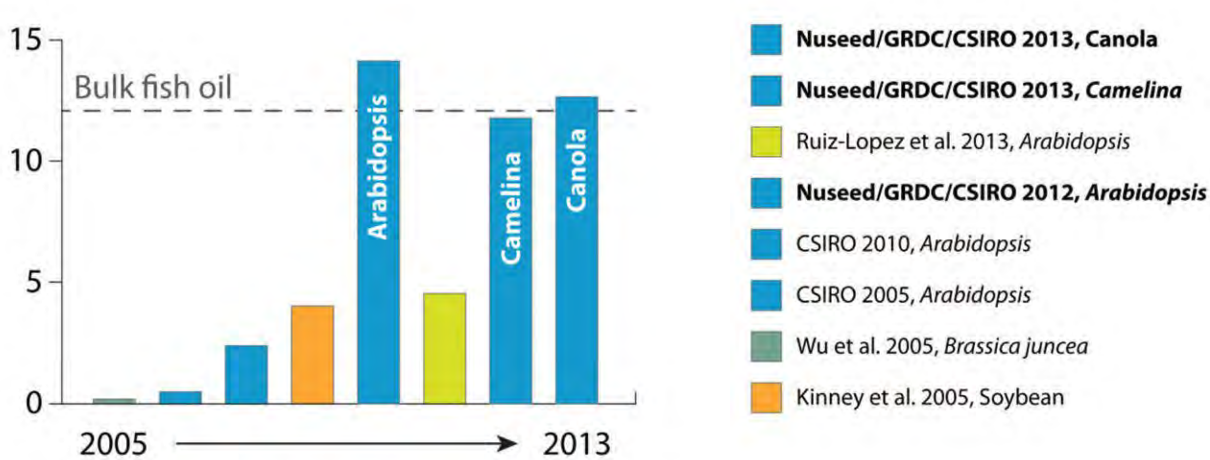

FIG. 2. Progress toward fish oil-like DHA levels in oilseeds.

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TABLE 2. Representative seed oil profile from transgenic DHA-producing Camelina together with a standard fish oil[a]

	Novel omega-3								Novel omega-6				
	OA	LA	ALA	SDA	ETA	EPA	DPA	DHA	GLA	DGLA	ARA	DTA	DPA6
Camelina oil	7.3	8.3	29.3	6.2	1.3	4.8	1.6	12.8	0.8	0.0	0.1	0.0	0.0
Fish oil	8.4	1.4	0.8	3.3	1.0	18.7	2.2	11.7	0.2	0.2	0.6	0.2	0.3

[a]The ω3/ω6 ratio on a percentage weight basis is 6:1 or 30:1 if only novel fatty acids are included. Abbreviations: OA, oleic acid; LA, linoleic acid; ALA, alpha linolenic acid; GLA, gamma linolenic acid; SDA, stearidonic acid; DGLA, dihomo-gamma linolenic acid; ETA, eicosatrienoic acid; ARA, arachidonic acid; EPA, eicosapentaenoic acid; DTA, docosatetraenoic acid; DPA, docosapentaenoic acid; DHA, docosahexaenoic acid.

& Development Corporation (GRDC) collaboration has produced seed from this species with a high ω3/ω6 ratio and very low levels of potentially undesirable intermediate fatty acids (Table 2). It is interesting to note that the engineered Camelina seed oil profile contained levels of DHA similar to those found in commodity fish oils. We can also report that fish oil-like levels of DHA have also been produced in our application crop, canola (Fig. 2, page 650).

THE FUTURE

Nuseed made a strategic decision in 2010 to pursue DHA production in canola as a way to supply the strong demand for LC-PUFA products. Key to this decision was the clear business opportunities and the strong scientific program at CSIRO, which already had support from the GRDC. Canola was chosen as the delivery vehicle for several reasons. Canola is an oilseed crop well adapted to many temperate growing regions, including in Australia, and therefore is a fully scalable source of long-chain ω3 oil. Canola seed has inherently high oil content (45%), meaning significant DHA yields can be achieved per hectare; current projections suggest that 1 Ha of DHA canola will replace 10,000 fish caught from the ocean (Petrie *et al.*, 2012; and references therein).

Nuseed has a well-established canola breeding and development program in Australia, with considerable experience in existing specialty oil markets (e.g., high-oleic Monola oil).

Based on recent progress in this collaboration, Nuseed intends to conduct field trials in Australia starting in 2014 subject to relevant regulatory approvals, with an anticipated commercial launch around 2018. Nuseed is currently engaging with potential downstream partners to develop the relationships and pipeline of activities that will see land plant-based long-chain ω3 oil enter the market shortly after this.

James R. Petrie is with the CSIRO Food Futures Flagship and based at CSIRO Plant Industry, Canberra, Australia, where he works on plant oil engineering. He has been part of Surinder Singh's group for 10 years and developed the recent DHA seed advances in CSIRO.

Peter D. Nichols is with the CSIRO Food Futures Flagship as part of the land plant long-chain omega-3 team and is based at the Division of Marine and Atmospheric Research in Hobart, Tasmania. He has been involved with long-chain ω-3 oils since the mid-1970s, has over a period of 20 years characterized the "good oil" in Australia's seafood, and has worked closely with the national marine oils and also aquaculture industries.

Malcolm Devine is the global innovation lead for Nuseed, the wholly owned seeds division of Nufarm Pty. Ltd. of Australia, where he is responsible for identifying new technologies and traits to support Nuseed's crop-breeding programs. Prior to joining Nuseed he held positions as professor of plant science at the University of Saskatchewan (Canada), research director at the National Research Council of Canada, and head of technology acquisition and licensing for the bioscience division of Bayer CropScience.

Surinder Singh is with the CSIRO Food Futures Flagship and based at CSIRO Plant Industry, Canberra, Australia. He is the leader of projects applying molecular biology of fatty acid synthesis and metabolic engineering to manipulate fatty acid composition to produce novel edible and industrial plant oils. His project team has developed the DHA-containing seed oil.

The authors thank the wider CSIRO Food Futures Flagship Omega-3 research team for their contributions.

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The use of carboxylate surfactants to enhance deinking in flotation processing during paper recycling

SURFACTANTS & DETERGENTS

- **During paper recycling, large ink particles are commonly removed by mixing the paper pulp with surfactant and then bubbling air into the solution. The ink preferentially adheres to the bubbles, which froth on the top of the liquid and can be skimmed off.**

- **The postulated mechanism for the ink's preferential adherence to the bubbles is that the fatty acid salts that are typically added to the paper pulp bind to the solid ink particles with the hydrophobic tail groups sticking outward, which in turn allows these now hydrophobic particles to adhere to the air bubbles and be removed to the surface as the air bubbles travel upward owing to buoyancy. For that to occur, the fatty acid salt must have a stronger affinity to adsorb to the ink than to adsorb to the paper fiber, but little is known about why this is so.**

- **Researchers at the University of Oklahoma (Norman, USA) recently examined this affinity to see if the experimental data in a model system support such a mechanism.**

Brian Grady

About 45 million tons (41 million metric tons) of paper and paperboard are recycled every year in the United States, which is a recycle rate over 63%. After pulping the paper into individual cellulosic fibers and removing foreign objects such as staples, large adhesive particles, and paper clips, the ink must be removed to create a much higher value product. Larger ink particles (e.g., 20–80 microns) are typically removed by a flotation process; surfactant is added to the mixture and air is bubbled through the solution. Much of the ink preferentially adheres to the bubbles, which rise to the top as a froth that can be easily removed via a skimming operation, as shown schematically in Figure 1. This process is different from a washing process, which is also used in deinking. In that case, washing is used to disperse smaller ink particles in water and remove the particles mechanically, accompanied by a screening operation to prevent the fibers from escaping. One key requirement in a flotation process is to add surfactant(s) that allow the ink to adhere to the bubble with a much higher probability than to the cellulosic paper fiber.

The most common surfactants used are sodium salts of fatty acids, to which is added calcium chloride, which effectively makes the system the calcium salt of the fatty acids since the binding efficiency of calcium is much larger than that of sodium. The postulated mechanism for any flotation separation involving surfactants is that the surfactant binds to the solid with the hydrophobic tail groups sticking outward, which in turn allows these now hydrophobic particles to adhere to the air bubbles and be removed to the surface as the air bubbles travel upward due to buoyancy. This mechanism implies a requirement for a stronger affinity of the fatty acid salt to adsorb to the ink than to the paper fiber. The goal of this study is to examine this affinity and see if the experimental data in a model system support this mechanism.

An adsorption isotherm for sodium octanoate on pulped office paper fiber is shown in Figure 2; the carbon chain of the fatty acid is eight carbon atoms long. Such graphs are critical to quantify the amount adsorbed (*y* axis) vs. the amount of surfactant remaining in solution after adsorption (*x* axis). The long increase in adsorption that is approximately linear, followed by a region where adsorption does not change with concentration, is typical for shorter-chain surfactants. The plateau is due to the critical micelle concentration (CMC); to a very good first approximation, adsorption does not change once micelles have formed. Commercially, a fatty acid salt with 12–16 carbon atoms is commonly used in flotation deinking processes. We used a much shorter carbon chain length because, under the conditions of the experiment, a longer-chain fatty acid would precipitate at a concentration far below the CMC. Precipitation would confound our results because we measured the isotherms by difference [(amount of surfactant added) – (amount present after adsorption)]; and if precipitation were to occur, we would not know how much surfactant was adsorbed and how much was precipitated. However, commercially, concentration at the lower end of the isotherm is important because precipitation occurs long before the CMC is reached when the surface is not fully covered with surfactant and hence our examination of the results will focus on this concentration region.

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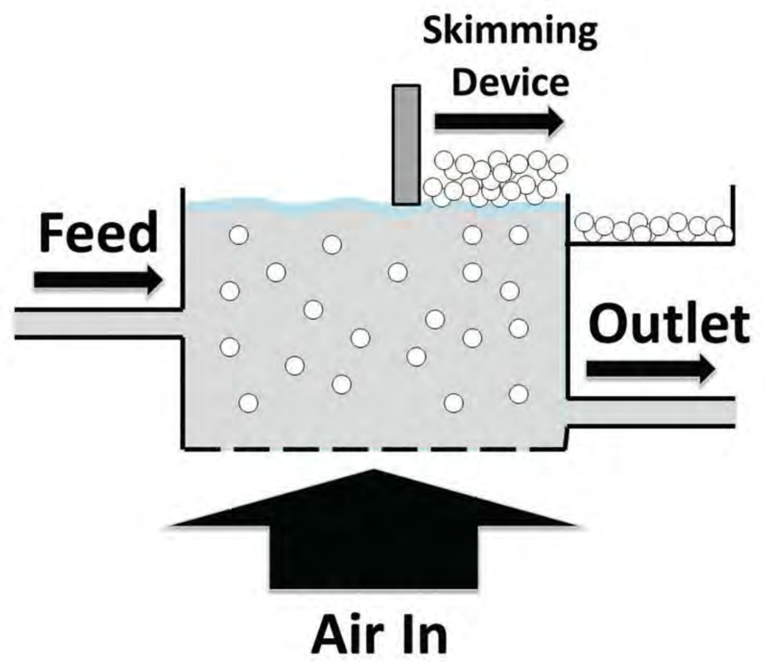

FIG. 1. Schematic of flotation deinking process.

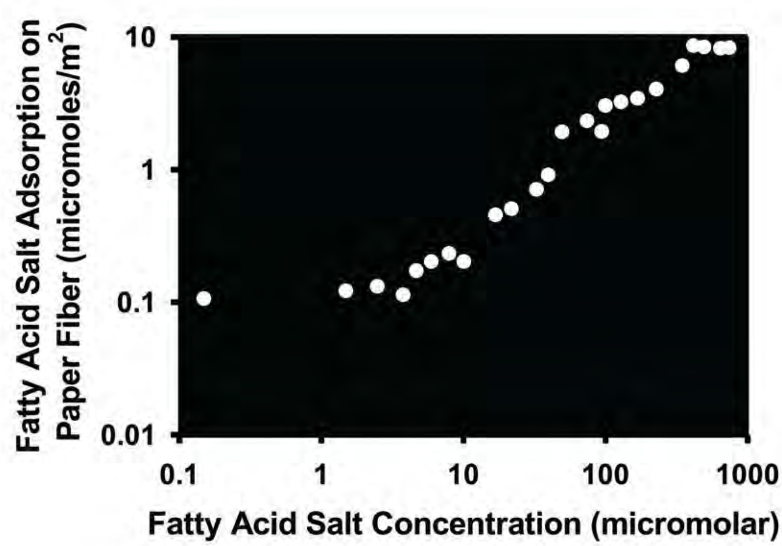

FIG. 2. Adsorption isotherm for sodium octanoate on pulped office paper.

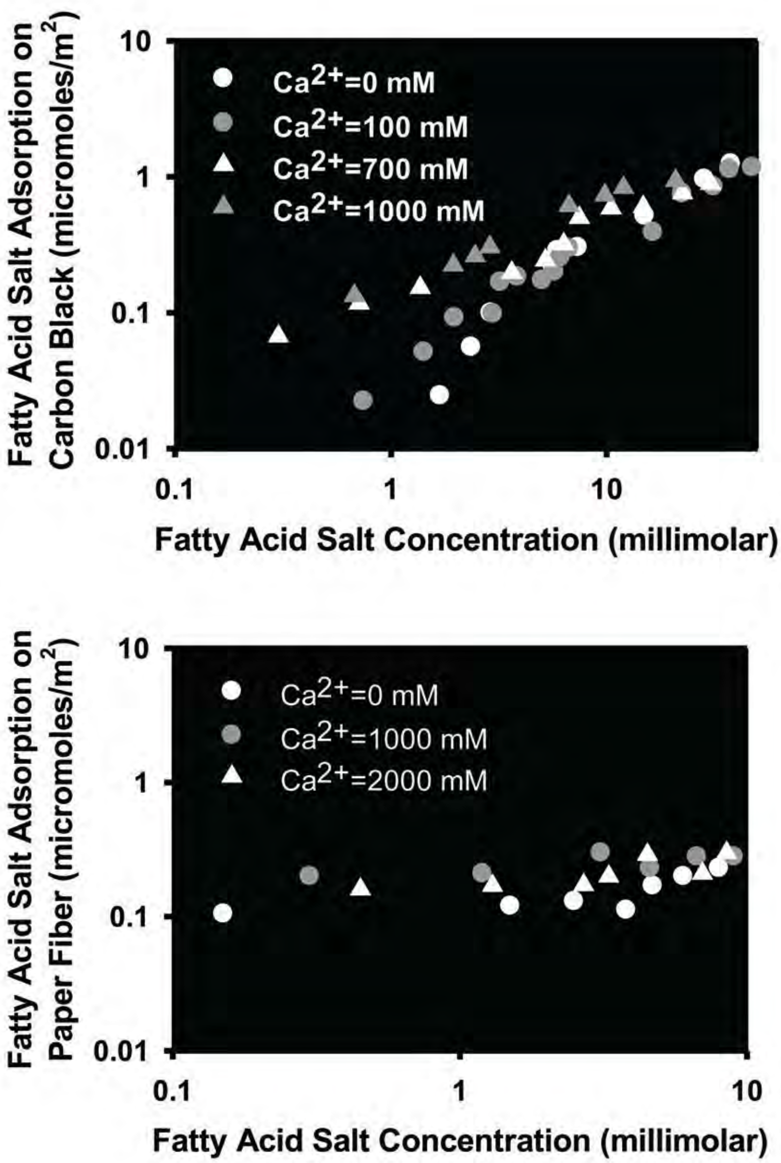

FIG. 3. Adsorption isotherms for printing ink carbon black (top) and pulped office paper (bottom) showing only low surfactant concentrations at different calcium chloride concentrations.

Figure 3 shows a comparison between adsorption of sodium octanoate (at low concentrations) on carbon black used in printing ink and on pulped office paper. Without the addition of calcium ion, the adsorptions are very similar, but with the addition of calcium, the adsorption on the carbon black increases substantially while that on the paper fiber increases much less, if at all. So we can conclude that calcium helps the air bubbles distinguish the two types of particles, carbon black and paper fiber. Further, according to this study, this separation only occurs at low surfactant concentrations. As the top plot of Figure 3 suggests, calcium has very little effect on adsorption on carbon black except at low concentrations. Finally, we also found that a common sulfate surfactant, sodium dodecyl sulfate, does not show the same dependence on calcium; that is, the presence calcium ion does not increase adsorption of this surfactant.

The concentrations of fatty acid used in commercial deinking are typically above the precipitation concentration, although with adsorption that statement may not be true in some cases (because adsorbed surfactant is not in solution and hence does not participate in the thermodynamic process leading to crystallization). Using easy-to-precipitate surfactants also provides a self-regulating type of process; given the varying solid surface area in a flotation deinker at any given time, the amount of adsorbed surfactant and hence the amount of surfactant in solution varies substantially. Precipitation limits the amount of surfactant adsorbed on the surface of the ink, which in turn does not allow a fully formed bilayer to form in water, thus making it easier for the particle to become hydrophobic in the presence of an air bubble. Of course, in some cases fatty acid salt precipitates will form, which must then be carried along with the froth and separated. Another reason that longer-chain fatty acids are used vs. short chains is related to the former creating a more hydrophobic particle, allowing for stronger and/or faster attachment to an air bubble.

Calcium is postulated to provide a bridge between the surface and the surfactant as shown schematically in Figure 4. Two outstanding scientific questions remain: (i) Why does calcium assist in adsorption for the case of the carboxylate anion but not for the case of the sulfate? It is well known that, everything else being equal, calcium is much more effective at precipitating surfactants containing carboxylates than those containing sulfates, and hence the most likely difference is that the two effects are related to one another and to the way in which calcium coordinates with carboxylate vs. sulfate. (ii) Why does calcium increase adsorption much more strongly on carbon black than on paper fiber? Since adsorptions at full coverage are roughly the same and correspond to bilayer coverage on an area basis, the adsorption in both cases is very likely to be head-down as depicted in Figure 4 and not tail-down (tail-down adsorption would have the surfactant molecules rotated 180° on the surface in Fig. 4). In other words, the simplest explanation, that adsorption is head-down on carbon black and tail-down on paper fiber, is not supported by the data. Another possibility is that calcium does not adsorb on the paper fiber surface; however, our measurements (not shown) indicate that in both cases all of the calcium atoms are adsorbed on the surface at the surfactant concentrations represented in Figure 3. However, at higher surfactant concentrations, calcium can be displaced by the surfactant only in the paper fiber case, but not in the carbon black case. Perhaps this observation is related to the mechanism of why calcium increases adsorption on the carbon black in a much stronger fashion than on paper fibers.

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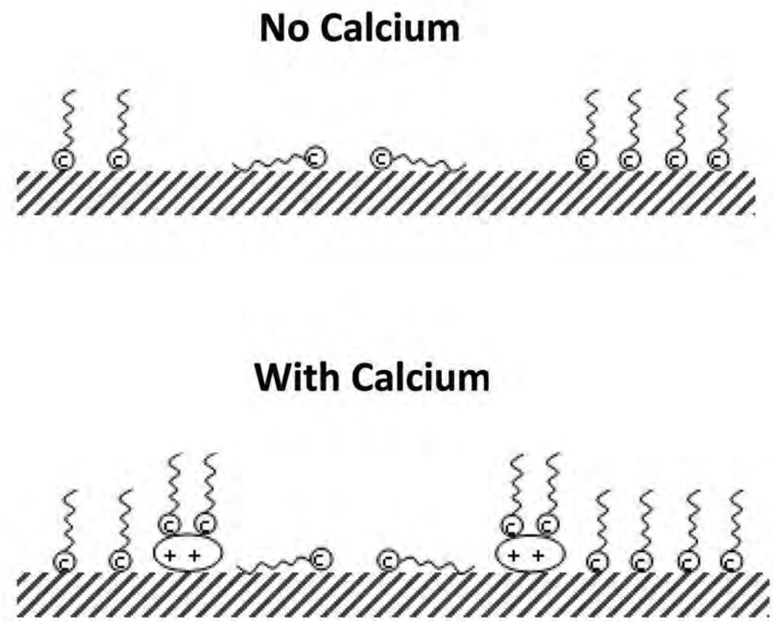

FIG. 4. Schematic of how calcium affects adsorption of surfactant. This schematic assumes air bubbles as the continuum; in water alone with head-down adsorption, the surfactant is arranged so that a bilayer is formed, that is, the head groups face the water phase. With air bubbles, the tail groups face the air since air is hydrophobic.

Do oil color scales make you see red . . . or yellow?

Eric Umbreit and Matthew Russell

FIG. 1. Lovibond Tintometer Model F colorimeter.

Among the many tests that need to be carried out on edible oils and fats during the refining process is the measurement of color. Color measurements are used not only to ascertain aesthetic quality but also as a means to optimize bleaching, deodorizing, and other production processes. Most, if not all, refined oils are sold on the basis of their color, and each type of oil will have its own "sell by color" instructions. So, it is necessary to monitor each stage of the refining process to establish whether the correct color has been reached.

- **Color measurement is a critical aspect of oil quality.**
- **Various scales for the measurement of edible oil color have been created by industry and have evolved. Unfortunately, apparent similarities between these color scales can mask critical differences, sowing a degree of confusion among decision makers.**
- **Understanding the evolution and differences between these scales will aid in selecting and communicating the correct color scale, eliminating confusion and costly misunderstandings.**

Some crude seed oils can have unexpectedly high pigmentation, often attributable to adverse growing conditions, such as too little or too much moisture or frost damage to the plant (Meloy, 1953). As a result the color tends to darken in storage. Early color measurement often can alert the refiner to potential expensive bleaching and blending problems. Mixing problem oil with "in spec" oils can compound the situation as the darkening effect is carried over (Fash, 1934). Obtaining color data regularly on oil suspected to be unstable would indicate its condition and help to avoid making incorrect decisions regarding blending.

There are many other reasons why color measurement of oils and fats is important, but ultimately it all relates to the cost of refining, the quality of the finished product, and what the product looks like to the end user. That end user may be a food producer who is

CONTINUED ON PAGE 662

How to reduce color communication problems

When comparing visual (subjective) to automatic (nonsubjective) color assessment, the fundamental differences between these methods need to be considered. Here are some basic steps to take to reduce color communication problems:

MAKE SURE THAT YOU HAVE A SYSTEMATIC, CONSISTENT, AND RELIABLE MEANS OF SAMPLE PREPARATION AND PRESENTATION

For example, when measuring liquids, are you using comparable, clean cells? Figure 2A shows the same liquid sample viewed across a range of cell path lengths. Figure 2B shows that, as path length changes, the perceived color of the samples will change significantly. Any visual or automatic methods' results would be influenced by this difference.

For example, with Lovibond RYBN Color, it is advisable that the depth of color never be greater than that which may be matched by a total of 20 Lovibond units.

The choice of pathlength will impact accuracy. Unless working to a particular specification, the optical path length of the cell used should be related to the color intensity of the sample—in a nutshell, the more intense the color, the shorter the pathlength.

When comparing with others, it is necessary to check that cell pathlength and type (optical glass, borosilicate, or plastic) are identical and the cells used are clean and undamaged.

CONFIRM THAT THE CORRECT COLOR SCALE IS SELECTED ON THE AUTOMATIC INSTRUMENT

As discussed, historically a number of scales are available that report red and yellow values. This is a common source of error. For example; a standard Model F reports Lovibond red, yellow, blue, and neutral units (RYBN).

An AF710 reports AOCS Tintometer scale in terms of red and yellow (RY). An automatic instrument may be configured to display both RYBN and RY. ■

FIG. 2A

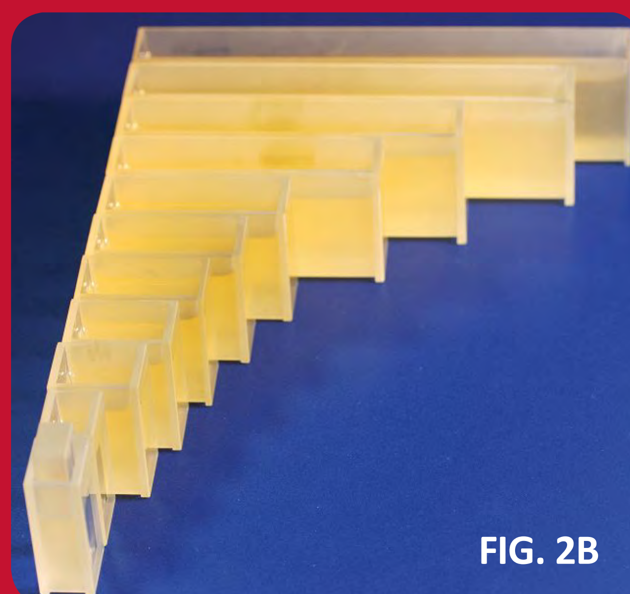

FIG. 2B

INFORMATION

- Meloy, G.W., *Cotton and Cotton Oil Press 44*(23):14 (1953).
- Fash, R.H., The effect of crude bollie cottonseed oil upon the color of refined oil from stored crude cottonseed oil, *Oil and Soap 11*:106–109 (1934).
- Zschau, W., Problems in bleaching differ with type of fat, *Inform 1*:638–644 (1990).
- Belbin, A.A., Color in oils, *Inform* 4:648–654 (1993).

TABLE 1. Review of various red/yellow color scales used in the edible fats and oils industry

Color scale	Method reference (if applicable)	Approximate development date	Approximate color measurement units/range[a]	Comments
Lovibond RYBN (Red, Yellow, Blue, Neutral)	AOCS Cc 13e-92, ISO 15305, MS 252: Part 16, IP17 Method A	Late 1800s	0–70 Red,0–70 Yellow,0–40 Blue, 0–3.9 Neutral	Used worldwide with the exception of North America
AOCS-Tintometer	AOCS Cc 13b-45 (the Wesson method), AOCS Cc 8d-55, AOCS Cc 13j-97	Mid-1900s	0–20 Red, 0–70 Yellow	Modified red + yellow version of the Lovibond RYBN color scale; used primarily in North America
AF-960	AOCS Cc 13e-92	Early 1980s	0–20 Red, 0–70 Yellow	Abridged red range and yellow Lovibond scale
BS684 (British standard modification of the Lovibond RYBN color scale)	BS 684 Section 1.14, ISO 15305, and AOCS Method Cc 13e-92	1977	0–70 Red, 0–70 Yellow, 0–40 Blue, 0–3.9 Neutral	Slightly modified version of Lovibond RYBN with colorless glass compensating slides in the sample field

[a]Color measurement range varies by instrument.

very aware of how the color of the oil could enhance or diminish that product's appearance.

An end user may not consciously notice the color of a cooking oil unless it appears different than usual; then, suddenly, color is all important. As soon as a color difference is perceived, the end user may infer that "different" means "not as good." Consequently, it is the goal of the edible oil plant production and quality processes to produce a consistent product in color—from plant to plant, lot to lot, and year to year.

COLOR MEASUREMENT METHODS AND COLOR SCALE CONFUSION

Color is a perceptual property in human beings. Color derives from the spectrum of light (distribution of light energy vs. wavelength) interacting in the eye with light-sensitive cells. In the human environment, materials are colored depending on the wavelengths of light they reflect or transmit. The visible color spectrum runs from red through to blue wavelengths, approximately 360–720 nm.

Three things are necessary to perceive color: (i) a light source, (ii) an object, and (iii) an observer/processor.

Colors are broadly described by descriptive words such as white, red, yellow, green, light, dark, bright, dull, and the like. However, each person describes and therefore defines an object's color differently.

As a result, objectively communicating a particular color to someone without some type of physical standard is difficult. Describing in words the precise color difference between two objects is very challenging.

A person's perceptions and interpretations of color and color comparisons are highly subjective. Fatigue, age, gender, and other physiological factors can influence color perception.

But even without such physical considerations, each observer interprets color based on their personal perspective, feelings, beliefs, and desires. For example, some people may convince themselves that a certain color match is within tolerance if they are under pressure to declare a color match as acceptable.

To quote the great 19th-century British scholar Lord Kelvin: "When you can measure what you are speaking about and express it in numbers you know something about it; but when you cannot express it in numbers your knowledge is of a meager and unsatisfactory kind."

With this in mind, over the years various methods have been developed to measure the color of edible oils and fats. Before the development of electronic instruments using multiple wavelengths and photodetectors, quantitative color measurements were completed by comparing the sample to known glass color standards.

One of these was the Tintometer® colorimeter, invented by Joseph Lovibond in England in the late 19th century. Lovibond was a brewer by trade—and he needed a method to consistently evaluate and regulate the color of his beer. The Tintometer uses a series of gradient red-, yellow-, blue-, and neutral-colored glasses. It is arranged with two adjacent fields of view, seen through the viewing tube, so that the product in the sample field and a white reflective surface in the comparison field are observed side by side, suitably illuminated. This is known as the Lovibond® color scale (AOCS Method Cc 13e-92.)

Lovibond's original Tintometer instrument concept is still in use around the world—and currently marketed as the Lovibond Tintometer Model F colorimeter (Fig. 1, page 660). This instrument uses 84 glass standards [in incrementally higher color intensity of Red (R), Yellow (Y), Blue (B), and Neutral (N) colors] to match the sample color visually. The Lovibond Tintometer colorimeter and its color standards quickly became a reliable tool for measuring and communicating the color description of many products including oils and fats. Small differences in colors can be measured and expressed in an easily understood and quantifiable way.

Early Tintometer instruments were supplied complete with a separate box of loose glass color standards each standard measuring 2″× ¾″ (5 cm × 2 cm). The red, yellow, and blue colors of the standards are achieved by adding metallic oxides to each batch before committing to the furnace. Different shades of light to dark colors are obtained by varying the amount of metallic oxides in each batch for permanency of color.

However, during World War II, the ability to supply precise glass color standards became tenuous owing to war efforts. To respond to demand, Lovibond distribution partners in the United States cut the 5 cm × 2 cm loose glass standards into thirds, not realizing that the color matching for the Lovibond standards was completed in the center of the lower third of each glass standard. The upper part was intended for labeling and handling and did not require calibration. Unfortunately, over time, this action caused a skewing of the original Lovibond color scale, resulting in market confusion. Simply stated, instruments would not read the same.

In 1958, to resolve the discrepancies that had resulted from dividing the glass color standards, AOCS and US Bureau of Standards (now called the National Institute of Standards and Technology) worked with Tintometer Ltd. to resolve the issue. As a result, a new color scale, a homogenization of the Lovibond glass color standards, was created. This new color scale was measured using the term N" color units.

The *Journal of the American Oil Chemists Society* [39(3):25, 1962] announced in 1962 that the new scale was finally finished and approved. It was named the "AOCS-Tintometer Scale" (or "Wesson Method," AOCS Method Cc 13b-45). The terms Lovibond and N" would be superseded by the AOCS-Tintometer scale in all results where compliance to Method Cc 13b-45 was required. Fundamentally, it is a modification of the Lovibond method—and focuses on the red and yellow colors—with no blue or neutral colors. With this instrument (called the Tintometer AF-710), it is possible to achieve a color match using only the red and yellow combination of standards. The lack of blue standards makes it necessary to ignore any difference in brightness and greenness. The visual-based instrument uses a physical gap between the sample and standard to account for brightness, unlike the Model F, which uses a neutral filter to make it duller. To this day, the AOCS-Tintometer scale is the most common color measurement scale used in the North American market.

Consequently, it should be pointed out that the red measurements of the Lovibond RYBN scale do not match those of the AOCS-Tintometer RY method. This creates confusion in the marketplace, as there is a tendency to report the "R" (red) value and not specify the color scale being used; 0.5 R on the Lovibond scale is not the same as 0.5 R on the AOCS-Tintometer scale. Much confusion can be averted merely by specifying/confirming the correct color measurement scale.

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Beyond the aforementioned Lovibond and AOCS-Tintometer scales, various color scale offshoots have evolved, such as the AF960 Lovibond scale, which is an abridged red and yellow Lovibond scale that was introduced on an early electronic colorimeter that had a "shortened" measurement range of 0–20 Red with the same 0–70 Yellow color range.

Another Lovibond RY color scale variant is BS684, which is a modification of the Lovibond Scale. Technically, BS684 is not a scale but a standard. The BS684 variant of the Lovibond scale is optimized for measuring animal and vegetable fats by adding colorless glass compensating slides in the sample field as well as utilizing a black sheath to stop the entrance of any external ambient light from the sides of the cell. The racks containing the red, yellow, and blue color standards are fitted with clear, colorless glasses—known as compensating slides—in the lower row of holes so that they cover the sample field. The reason for the use of compensating slides is as follows: when light passes through a glass filter, a small percentage is lost at each of the glass surfaces owing to scattering and refraction, in addition to that which is lost through internal transmission due to the color of the glass. The result is a loss of brightness in the comparison field. To illustrate, the visual difference in color between 1.0 and 1.1 red is more noticeable than the difference between 0.8 and 0.9 red. The difference in saturation is similar between the two sets of filters, but the difference in brightness is down by about 8% for the higher-value filters due to the effect of light loss at the extra glass surfaces used to make up 1.1 red (a 1.0 red filter and a 0.1 red filter).

Compensating slides fitted in the racks counteract this brightness difference as they introduce the same number of glass surfaces into the sample field as are used in the comparison field to achieve a color match.

It should also be noted that, due to the high stability of glass standards, many instruments in the field are often of a venerable age. Unfortunately, over the decades they have often been modified and in many cases provide results that have drifted far from the standards. It is advisable such units be checked for compliance with calibrated glass or liquid standards.

Table 1 (page 662) details and summarizes these various color scales.

DEVELOPMENT OF ELECTRONIC COLOR MEASUREMENT INSTRUMENTS

As technology advanced, it became possible to measure color by using an electronic optical system, such as a colorimeter or spectrophotometer. However, this process was more challenging than would appear at first review. For instance, due to the vagaries of the human eye, how does one get an electronic photodetector to match the reading that most observers would see if they used the glass standards? Since each person sees color differently, in effect, the instrument would have to "average" the values that a range of observers would report for a specific sample with a particular color scale. This task was eventually completed by generating a massive amount of absorbance data for each of the color standards using the full spectrum of color wavelengths.

Regardless of whether an eye-based glass standard method or a modern electronic instrument is used, it is critical to specify which color scale is being measured (i.e., Lovibond, AOCS Tintometer, etc., including method reference), how samples have been prepared, and cell path length.

Eric Umbreit has been in the scientific instrumentation industry for over 15 years. He has a bachelor's degree from Colorado State University (Ft. Collins, USA) and a master's from Santa Clara University (California, USA). His email address is e.umbreit@tintometer.com.

Matthew Russell has over 15 years' experience in the field of color measurement having worked for GretagMacbeth, X-Rite, and Lovibond Tintometer. He has an honors degree in chemistry from the University of Manchester and a master's degree from the University of Manchester Institute of Science and Technology in the United Kingdom. His email address is m.russell@tintometer.com.

PEOPLE/INSIDE AOCS

Letter from the president

Our society got its start in 1909 as a group of US cottonseed industry professionals looking to establish common means of analysis for their products. From this humble beginning, AOCS has steadily grown its scope of interest and its geographical reach.

Today, AOCS is a unique society that serves a very diverse, yet connected group of people and organizations whose collaborative efforts improve the quality of human life in fundamental ways. Whether you contribute by processing oilseeds into meal and oil, modifying meal into higher-value protein products, modifying oils or fats into higher-value edible and industrial products, improving lipid quality, finding new edible applications, improving health and nutrition, applying phospholipids derived from oil, producing sustainable surfactants and cleaning products, discovering new biotechnology applications, or determining the latest analysis methods, AOCS gives you the professional development, networking opportunities, and access to information you need to make the most of your efforts .

We now have over 4,000 members and countless more interested individuals utilizing AOCS products and services. These members and friends span the globe. The Official Methods of AOCS are used globally to measure quality and act as a basis for fair trade. Trustworthy technical knowledge is distributed globally via consortia agreements and our website. AOCS meetings have no intellectual or geographic boundaries. Since April 2013, we have held meetings in Ukraine, Canada, India, and Chile. AOCS is truly a global society and the hub of knowledge and networking for professionals in more than a dozen interest areas, from health and nutrition to surfactants and detergents.

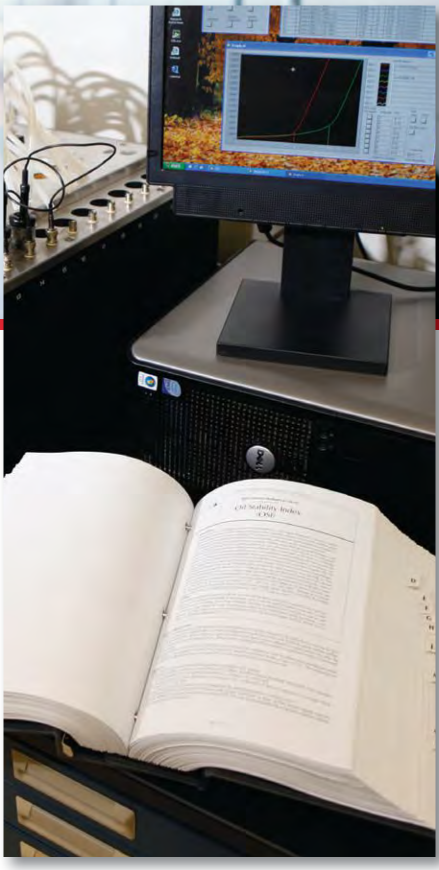
So where do we go from here? No organization can rest on its past successes. It is our vision to continue to grow AOCS, and to do so in a strategic and fiscally responsible manner. While we have good participation in the Americas and Europe, we have a lot of room for progress throughout Asia. After all, Asia is the population center of the world and is therefore central to AOCS' mission to enrich the lives of people everywhere. Consequently, our strategic plan includes objectives for partnering with allied organizations in new ways that increase participation in this region.

Another key strategic initiative is to grow global participation in AOCS though virtual means. We now live in a world vastly different from the world of just 20 years ago. Our smart phones keep us continuously connected and updated regardless of where we are. There is an accelerating demand for accessing people and knowledge at rapid speed. As our members and other interested individuals struggle with these demands, AOCS needs to be the hub that connects these people and enables rapid knowledge transfer. While *Inform* magazine and occasional meetings might have been sufficient 20 years ago, the next 20 years will require us to do much more. In 2014, AOCS will roll out "INFORM|Connect," the virtual global hub that will link those specifically interested in AOCS-related topics to one another for rapid knowledge transfer. Today we are finalizing the implementation of Personify, a new association management system, which will serve as the platform for "INFORM|Connect." This is an exciting development and one that will help AOCS meet the rapidly changing needs of our members and interested individuals throughout the world.

The future of AOCS, just as its past, is fully dependent on the contributions of its people and the organizations that support us. I am always impressed by the many members and interested individuals who, despite their hectic schedules, provide AOCS with their valued time. I am also thankful to the many people and organizations that provide AOCS with both talent and treasure. To enable progress we need more people and organizations to support AOCS. If you and the organization you work for have found AOCS of value and can increase your involvement, please contact us. We would love to have your contributions as, together, we strive to enrich the lives of people everywhere.

Timothy G. Kemper
AOCS President, 2013–2014

SAVE
in December on *AOCS Methods*



The *Official Methods and Recommended Practices of the AOCS*, 6th Edition, 3rd Printing is **ON SALE** for the month of December.

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TECHNICAL SERVICES AOCS

2014 AOCS Annual Meeting & Expo: San Antonio is set to inspire

San Antonio Convention & Visitors Bureau

Deep in the heart of Texas, San Antonio's great facilities and attractions, bold culture, and historic legacy make the city an ideal destination for attendees of the 105th AOCS Annual Meeting & Expo, May 4–7, to make Texas-sized memories as they broaden their knowledge, enhance their careers, and connect with professionals from all over the world.

The historic city is home to the famous River Walk—one of the top visitor destinations in Texas, and a cornerstone of the state's robust meetings industry. Also known as the "world's largest hotel lobby," the five-mile network of walkways lined by bars, shops, and restaurants is the perfect place for networking, nightlife, and entertainment.

Located right on the River Walk, the Henry B. Gonzalez Convention Center, headquarters for the AOCS meeting, features plentiful natural indoor lighting and beautiful outdoor venues such as the River Walk Grotto, Waterfall Patio, and Plaza Mexico. The center is a short stroll to numerous hotel rooms, restaurants, and attractions—all of which can be conveniently reached from the street level. And, for those who'd rather ride than walk, river taxis and trolley cars are fun, unique options.

Great weather makes San Antonio a top destination as well. The average temperature in May is 77° Fahrenheit (25°C)—perfect for taking in some of the historic sites. No trip to San Antonio is complete without a visit to The Alamo. This former mission was the site on March 6, 1836, of a battle between nearly 200 US defenders, who had taken The Alamo in 1835, and Mexicans intent on recapturing their territory; none of the US defenders survived. Four other Spanish Colonial Missions can be found nearby on the Mission Reach of the newly expanded River Walk.

Dining in San Antonio is foodie heaven! In addition to favorite Tex-Mex options such as chile con carne, chimichangas, and fajitas, attendees can sample innovative dishes at the many new restaurants that have sprung up in the Pearl Brewery and Southtown areas, making the city an increasingly popular culinary destination.

105th AOCS Annual Meeting & Expo
May 4–7, 2014
San Antonio, Texas, USA
AnnualMeeting.aocs.org
Program and registration information available in early 2014

The roots of the local culture, deriving from Mexico, Germany, and the Old West, combine to provide an "only in San Antonio" experience as evidenced through the visual arts. Several unique museums feature special collections, such as Latin American Art and Western Art.

Fantastic year-round weather and gently rolling Hill Country terrain make San Antonio an exciting golf destination. More than 50 courses provide a wide range of styles and prices for all levels of golfers. The city also boasts several amusement parks, including two theme parks: SeaWorld San Antonio, which is the world's largest marine life park, and Six Flags Fiesta, which offers outstanding entertainment and amusement ride options. Morgan's Wonderland, the world's first fully accessible amusement park, offers fun for all.

No matter what AOCS meeting attendees choose to do, they will be warmly welcomed by the hospitality of San Antonians and enveloped by in the rich culture of the city. San Antonio has been a colony of Spain, a territory of Mexico, a part of the Republic of Texas, and, finally, a state in the United States. Relics and tales from this iconic past linger everywhere—from The Alamo to places like La Villita and Market Square —guaranteeing unforgettable Texas-sized memories.

PATENTS

Use of carboxylic acid esters as a fragrance substance

Panten, J., *et al.,* Symrise AG, US8389466, March 5, 2013

A description is provided of the use of certain carboxylic acid esters as a fragrance substance, preferably as a fragrance substance for conveying, modifying, and/or intensifying one, two, or all the fragrance notes fruity and green, preferably both the fragrance notes fruity and green.

Production of acid soluble soy protein isolates ("S700")

Schweizer, M., *et al.,* Burcon Nutrascience (MB) Corp., US8389040, March 5, 2013

A soy protein product having a protein content of at least about 60 wt% (N·6.25) d.b., preferably an isolate having a protein content of at least about 90 wt% (N·6.25) d.b., is formed by extracting a soy protein source with a salt solution, preferably aqueous sodium chloride solution, to form an aqueous protein solution having a pH of about 1.5–11, preferably about 5 to about 7 and separating the resulting aqueous protein solution from residual soy protein source. The protein concentration of the aqueous protein solution is increased to about 50–400 g/L while the ionic strength is maintained substantially constant by using a selective membrane technique. The resulting concentrated protein solution is optionally diafiltered and a calcium salt, preferably calcium chloride, is added to the concentrated and optionally diafiltered protein solution to a conductivity of 15 mS to about 85 mS. Precipitate formed as a result of the calcium salt addition is removed and the resulting clarified retentate is diluted into about 2 to about 20 volumes of water prior to acidification to a pH of about 1.5 to about 4.4 to produce an acidified clear protein solution. The acidified clear protein solution is then concentrated and optionally diafiltered and optionally dried. Variations of this procedure can be used to produce a soy protein product that is soluble, transparent, and heat stable in acidic aqueous environments.

Fractionation method of 1, 3-disaturated-2-unsaturated triglyceride

Arimoto, S., *et al.,* The Nisshin OilliO Group, Ltd., US8389754, March 5, 2013

The present invention discloses a method of producing triglycerides rich in XOX [where X = a saturated fatty acid residue; O = oleoyl group; L = linoleoyl group] fat and/or XLX fat, which comprises the steps of heating and dissolving triglycerides (XOX fat and/or XLX fat) which comprise 20–60 mass% of a triglyceride having a saturated fatty acid residue on each of the first and third position and an oleoyl group and/or a linoleoyl group on the second position in total triglycerides in the presence of 1–30 mass% of a fatty acid lower alkyl ester; and then cooling the mixture to precipitate crystals and conducting solid-liquid separation. This method is a more efficient and industrially suitable fractionation and production method of fats and oils which are rich in a triglyceride (XOX fat and/or XLX fat) having a saturated fatty acid residue on each of the first and third position and an oleoyl group and/or linoleoyl group on the second position.

Amorphous adsorbent, method of obtaining the same and its use in the bleaching of fats and/or oils

Ortiz Niembro, J.A., *et al.,* Süd-Chemie AG, US8394975, March 12, 2013

The invention relates to a method for producing an adsorbent, in particular a bleaching earth, wherein a clay material having: a surface area of 180–300 m^2/g; a total pore volume of 0.5–0.7 mL/L; wherein at least 60% of the total pore volume is provided by pores having a pore diameter of at least 140 Å, at least 40% of the total pore volume is provided by pores having a pore diameter of less than 250 Å, and at least 15% of the total pore volume is provided by pores having a pore diameter of 140–250 Å; and said clay material having an amorphous structure according to X-ray diffraction data; is activated by an activation procedure. Further, the invention relates to an adsorbent as obtained by the method and a method for purification of oils, fats, and biofuels.

Neutralization process

Weismantel, M., *et al.,* BASF SE, US8410235, April 2, 2013

The invention relates to a neutralization process in which at least one ethylenically unsaturated carboxylic acid is neutralized at least partly with a base and at least one stream of the neutralization is determined continuously, and also to an apparatus for carrying out the process.

Water-based mud lubricant using fatty acid polyamine salts and fatty acid esters

Xiang, T., and R.A.M. Amin, Baker Hughes Inc., US8413745, April 9, 2013

Water-based drilling mud lubricants using a blend of fatty acid polyamine salts and fatty acid esters give synergistically better lubricity results than either component used separately. For example, the blends with different ratios of fatty acid diethylenetriamine salt and fatty acid methyl ester demonstrate much better lubricity in water-based drilling fluids than those where only fatty acid diethylenetriamine salt or fatty acid methyl ester are separately used. The amines in fatty acid amine salt might also include other polyamines, such as butanediamine pentamethylenediamine, spermidine, spermine, propylene diamine, and propylene polyamines. The fatty acid esters might also include fatty acid ethyl ester, fatty acid glycerol ester, and fatty acid trimethylolpropane ester. The carbon numbers of the fatty acids used to make the components in the lubricant blend may range from C4 to C28.

IN MEMORIAM

WILLIAM E. LINK

Former AOCS President William Edward Link died on August 10, 2013, in Columbus, Ohio, USA, at the age of 92. Bill is survived by Betty, his wife of 66 years; two daughters, three grandsons, and two great grandsons.

Link was born in Ironwood, Michigan, USA. He received his bachelor's degree in chemistry from Northland College, Ashland, Wisconsin, in 1942 and then joined the US Army, Chemical Warfare Service. He served on active duty in World War II from 1942 to 1946, participating in a 30-month campaign from Sicily to Salzburg, Germany, during which he was awarded the Bronze Star Medal. At the end of the war, he had achieved the rank of captain, and he continued afterward in the Reserves.

He married Betty Jane Senn in 1947 and took a position as an assistant professor of chemistry at Northland College 1947–1952. Link returned to school at the University of Wisconsin, Madison, where he received his M.S. degree in 1951 (thesis topic: "Studies on the quantitative determination of the autoxidation and the peroxide number of rancid fatty oils") and his Ph.D. under Henry Schuette in analytical chemistry in 1954 ("Studies on the minor components of rye germ oil").

His first position after graduate school was with Archer Daniels Midland in Minneapolis, Minnesota. After Ashland Oil Co. acquired ADM Chemicals in 1967, he moved to Columbus, Ohio, where he was the analytical chemistry group leader for the newly formed Ashland Chemical Co. When Schering AG acquired Ashland Chemical's R&D group in 1979, Dr. Link became vice president and director of research for the newly formed Sherex Chemical Co. He retired from Sherex in 1987.

Link's activities in AOCS were many. He served on a number of different committees, including membership, publication, instrumental techniques committee, and standards committee; and he was editor of AOCS *Official and Tentative Methods* in 1971. His first national office was as a member at large of the Governing Board (1971–1972). He was elected secretary for 1973–1974, vice president in 1974–1975, and president 1975–1976. He continued on the Governing Board until 1980. Link was general chairman of the World Conference on Oleochemicals in Montreux, Switzerland, in 1983, and co-chairman of the World Conference on Oleochemicals into the 21st Century in Kuala Lumpur, Malaysia, in 1990.

NED MILES ROCKWELL

Ned Rockwell, an AOCS member since 1981, died on May 17, 2013, in Lake Bluff, Illinois, USA, after a brief illness. He was 56 years old. His wife of 29 years, Amy (Hartzell), survives, as well as his children, Ben, John, and Rachel, all of Lake Bluff; his mother, and his sister.

He grew up in Gary, Indiana, USA, and graduated from Purdue University (West Lafayette, Indiana) in 1979 with a B.S. in chemistry. Later he received an M.S. in chemical engineering from the Illinois Institute of Technology (Chicago) in 1986 and M.B.A. from Northwestern University's Kellogg School of Management (Skokie, Illinois; 1990).

Rockwell started with Stepan Chemical Co. right out of undergraduate school as a process chemist. He worked for the company for 21 years, with several years as the global head of their agricultural chemical business.

He then moved on to become president and CEO of ABR, LLC, an early-stage biotechnology company focused on specialty products derived from its patent portfolio of mycological processes and applications.

At the time of his death he was executive vice president for corporate for Pons Pharma, Inc. (Lake Bluff, Illinois), an early-stage pharmaceutical company focused on bringing products to market that help children comply with their drug therapies. He was also principal of Rockwell Business Consulting, LLC.

Rockwell participated in the USA Section of AOCS (formerly the North Central Section), and was vice president of the North Central Section in 1995–1996. ■

Production of soluble soy protein product from soy protein micellar mass ("S300/S200")

Segall, K.I., *et al.*, Burcon Nutrascience (MB) Corp., US8409654, April 2, 2013

A soy protein product having a protein content of at least 60 wt% (N·6.25) dry weight, preferably a soy protein isolate having a protein content of at least about 90 wt% (N·6.25) d.b., is formed by a soy protein micellar mass production route. The supernatant from the coalesced protein micellar mass may be processed to recover additional quantities of soy protein product. The soy protein product may be used for a fortification of soft drinks and sports drinks.

Enzymatic modification of oil

Kralovec, J.A., *et al.*, Ocean Nutrition Canada Ltd., US8420349, April 16, 2013

The disclosed subject matter relates generally to a method for modifying oil, and specifically to a process for increasing the concentration of polyunsaturated fatty acid in an oil composition.

Patent information is compiled by Scott Bloomer, a registered US patent agent with Archer Daniels Midland Co., Decatur, Illinois, USA. Contact him at scott.bloomer@adm.com.

EXTRACTS & DISTILLATES

Rapid determination of olive oil oxidative stability and its major quality parameters using vis/NIR transmittance spectroscopy

Cayuela Sánchez, J.A., *et al.*, *J. Agric. Food Chem. 61*:8056–8062, 2013.

This paper reports the determination of the olive oil stability index (OSI) by multivariate models from the visible (vis) and near-infrared spectrum (NIRS). The technique proposed is rapid and nondestructive and can be used as a multiparametric method. Moreover, it does not require specific instrumentation, and it is environmentally friendly. The determination of the OSI using the Rancimat instrument was used as a reference method. Predictive (vis/NIRS) models were obtained from partial least squares (PLS) for the OSI, showing satisfactory performance in independent tests as proven by the R^2 values of 0.93 and 0.94 from the calibration and the residual predictive deviation (RPD) of the external validations of 3.30 and 3.00, respectively. Predictive models for the determination of free fatty acids, peroxide value, and conjugated dienes were also developed, and their satisfactory performances were demonstrated by RPD values of 3.14, 2.84, and 2.56; hence, its multiparametric determination together with OSI would be possible.

Effect of deodorization of camelina (*Camelina sativa*) oil on its phenolic content and the radical scavenging effectiveness of its extracts

Hrastar, R., *et al.*, *J. Agric. Food Chem. 61*: 8098–8103, 2013.

The influence of deodorization parameters [temperature (T), steam flow (S), time (t)] on the phenolic content and radical scavenging effectiveness (RSE) of methanolic extracts of camelina oil was investigated and analyzed by response-surface methodology (RSM). The phenolic content can be considered to be a linear function of all three parameters. A positive linear relationship between the content of phenolic compounds in deodorized oils and RSE was observed. Deodorization at 210°C with a steam flow of 3 mL/h for 90 min resulted in the best preservation of phenolics, amounting to 29.9 mg/kg. The lowest reduction from RSE of 12.4 μM Trolox equivalents (TE)/g oil for the crude oil was observed for oil treated at 195°C and 18 mL/h for 60 min with RSE of 10.1 μM TE/g oil. The lack of correlation between RSE or total phenolic content and oxidative stability of the deodorized oils suggests that antioxidants in scavenging radicals react by different mechanisms, depending on radical type and reaction medium.

Liposomes as vehicles for lutein: preparation, stability, liposomal membrane dynamics, and structure

Tan, C., *et al.*, *J. Agric. Food Chem. 61*:8175–8184, 2013.

Lutein was loaded into liposomes, and their stability against environmental stress was investigated. Subsequently, these findings were correlated with the interactions between lutein and lipid bilayer. Results showed that the liposomes with loaded lutein at concentrations of 1 and 2% remained stable during preparation, heating, storage, and surfactant dissolution. However, with further increase in the loading concentration to 5 and 10%, the stabilization role of lutein on membrane was not pronounced or even opposite. Membrane fluidity demonstrated that at 1 and 2%, lutein displayed less fluidizing properties both in the headgroup region and in the hydrophobic core of the liposome, whereas this effect was not significant at 5 and 10%. Raman spectra demonstrated that lutein incorporation greatly affected the lateral packing order between acyl chains and longitudinal packing order of lipid acyl chains. These results may guide the potential application of liposomes as carriers for lutein in nutraceuticals and functional foods.

Olive oil has a beneficial effect on impaired glucose regulation and other cardiometabolic risk factors. Di@bet.es study

Soriguer, F., *et al.*, *Eur. J. Clin. Nutr. 67*:911–916, 2013.

Despite the marked increase in cardiovascular risk factors in Spain in recent years, the prevalence and incidence of cardiovascular diseases have not risen as expected. Our objective is to examine the association between consumption of olive oil and the presence of cardiometabolic risk factors in the context of a large study representative of the Spanish population. A population-based, cross-sectional, cluster sampling study was conducted. The target population was the whole Spanish population. A total of 4,572 individuals aged ≥18 years in 100 clusters (health centers) were randomly selected with a probability proportional to population size. The main outcome measures were clinical and demographic structured survey, lifestyle survey, physical examination (weight, height, body mass index, waist, hip, and blood pressure) and oral glucose tolerance test (OGTT) (75 g). Around 90% of the Spanish population uses olive oil, at least for dressing, and slightly fewer for cooking or frying. The preference for olive oil is related to age, educational level, alcohol intake, body mass index, and serum glucose, insulin, and lipids. People who consume olive

CONTINUED ON PAGE 672

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- Structures and polymorphic transitions of triacylglycerols, SOS and POS thin films: a study on temperature dependence, Shimizu, K., Y. Uozaki, K. Nozaki, M. Uenaka, H. Terauchi, and I. Takahashi
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- Improved synthesis of monopalmitin on a large scale by two enzymatic methods, Wang, X., X. Wang., Q. Jin, and T. Wang
- Selective synthesis of glyceryl tris[9,10-(*threo*)-dihydroxyoctadecanoate], Elkin, I., and P. Hildgen
- Characterization of carnauba wax inorganic content, Dantas, A.N.S., T.A. Magalhães, W.O. Matos, S.T. Gouveia, and G.S. Lopes
- A comparison of the thermo-physical behavior of engkabang (*Shorea macrophylla*) seed fat–canola oil blends and lard, Nur Illiyin, M.R., J.M.N. Marikkar, M. Shuhaimi, B. Mahiran, and M.S. Miskandar
- Fatty acid composition in ergosteryl esters and triglycerides from the fungus *Ganoderma lucidum*, Deng, Z.-L., J.-P. Yuan, Y. Zhang, X.-M. Xu, C.-F. Wu, J. Peng, and J.-H. Wang
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- Physicochemical properties and minor lipid components of soybean germ, Yu, D., W. Elfalleh, S. He, Y. Ma, L. Jiang, L. Li, L. Hu, and J. Zhang
- Antioxidant properties of three aromatic herbs (rosemary, thyme and lavender) in oil-in-water emulsions, Gallego, M.G., M.H. Gordon, F.J. Segovia, M. Skowyra, and M.P. Almajano
- Comments on a method for estimating cloud point and cold filter plugging point of microalgal oil fatty acid methyl esters, Iyer, R.
- The role of peracetic acid in bloodmeal decoloring, Hicks, T.M., C.J.R. Verbeek, M.C. Lay, and M. Manley-Harris
- Using a strong anion-exchange resin to deacidify red palm oil, Cuevas, M.S., T.M. Deboni, P. M. Neto, F.S. Damasceno, R.V. Mota, L.H.M. da Silva, C.E.C. Rodrigues, and A.J.A. Meirelles

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- Lipid-modulating treatments for mixed dyslipidemia increase HDL-associated phospholipase A_2 activity with differential effects on HDL subfractions, Kei, A., E. Liberopoulos, C. Tellis, M. Elisaf, and A. Tselepis
- Inhibition of stearoyl-CoA desaturase 1 reduces lipogenesis in primary bovine adipocytes, Kadegowda, A.K.G., T.A. Burns, S.L. Pratt, and S.K. Duckett
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- Headspace volatile oxylipins of Eastern Himalayan moss *Cyathophorella adiantum* extracted by sample enrichment probe, Mitra, S., B.V. Burger, and M. Poddar-Sarkar
- A trichome-specific linoleate lipoxygenase expressed during pyrethrin biosynthesis in pyrethrum, Ramirez, A.M., T. Yang, H.J. Bouwmeester, and M.A. Jongsma
- Antidyslipidemic and antioxidant effects of novel lupeol-derived chalcones, Srivastava, S., R. Sonkar, S.K. Mishra, A. Tiwari, V. Balramnavar, S. Mir, G. Bhatia, A.K. Saxena, and V. Lakshmi
- Unusually high levels of n-6 polyunsaturated fatty acids in whale sharks and reef manta rays, Couturier, L.I.E., C.A. Rohner, A.J. Richardson, S.J. Pierce, A.D. Marshall, F.R.A. Jaine, K.A. Townsend, M.B. Bennett, S.J. Weeks, and P.D. Nichols
- Rapid detection and quantification of triacylglycerol by HPLC–ELSD in *Chlamydomonas reinhardtii* and *Chlorella* strains, Kobayashi, N., E.A. Noel, A. Barnes, J. Rosenberg, C. DiRusso, P. Black, and G.A. Oyler
- Quantification of phospholipids classes in human milk, Giuffrida, F., C. Cruz-Hernandez, B. Flück, I. Tavazzi, S.K. Thakkar, F. Destaillats, and M. Braun

oil (vs. sunflower oil) had a lower risk of obesity [odds ratio (OR) = 0.62 (95% confidence interval (CI) = 0.41–0.93, P = 0.02)], impaired glucose regulation [OR = 0.49 (95% CI = 0.28–0.86, P = 0.04)], hypertriglyceridemia [OR = 0.53 (95% CI = 0.33–0.84, P = 0.03)], and low high-density lipoprotein cholesterol levels [OR = 0.40 (95% CI = 0.26–0.59, P = 0.0001)]. The results show that consumption of olive oil has a beneficial effect on different cardiovascular risk factors, particularly in the presence of obesity, impaired glucose tolerance, or a sedentary lifestyle.

Nutraceutical nanoemulsions: influence of carrier oil composition (digestible versus indigestible oil) on β-carotene bioavailability

Rao, J., *et al.*, *J. Sci. Food Agric.* 93:3175–3183, 2013.

Carotenoids, such as β-carotene, are widely used in foods and beverages as natural colorants and nutraceuticals. We investigated the influence of carrier oil composition (ratio of digestible to indigestible oil) on the physical stability, microstructure, and bioaccessibility of β-carotene nanoemulsions using a simulated gastrointestinal tract model. β-Carotene nanoemulsions (d < 150 nm) were formed by high-pressure homogenization using sucrose monoester and lysolecithin as emulsifiers, and mixtures of corn oil (digestible) and lemon oil (indigestible) as the lipid phase. All of the nanoemulsions underwent extensive droplet aggregation under mouth, stomach, and small intestine conditions. The extent of free fatty acid production in the small intestine increased as the amount of digestible oil in the droplets increased. The bioaccessibility of β-carotene also increased with increasing digestible oil content, ranging from ~5% for the pure lemon oil system to ~76% for the pure corn oil system. This effect was attributed to the ability of mixed micelles formed from triglyceride digestion products (free fatty acids and monoglycerides) to solubilize β-carotene. This study provides important information for developing effective delivery systems for lipophilic bioactive components in food and beverage applications.

More than biofuels—potential uses of microalgae as sources of high-value lipids

Chang, K.J.L., *et al.*, *Lipid Technol.* 25:199–203, 2013.

Cultivation of microalgae has potential in producing a feedstock for biofuels and, in addition, high-value lipid bioproducts such as long-chain ($\geq C_{20}$; LC) omega-3 oils, carotenoid pigments, and squalene as well as other non-lipid materials including exopolysaccharide. The high-value LC omega-3 oils have been conventionally sourced from fish. This paper provides a perspective on our recent study of the heterotrophic growth of thraustochytrids for their wider biotechnological potential, including as a source of a range of higher-value lipids in addition to biofuels.

More Extracts & Distillates can be found in this issue's supplement (digital and mobile editions only).

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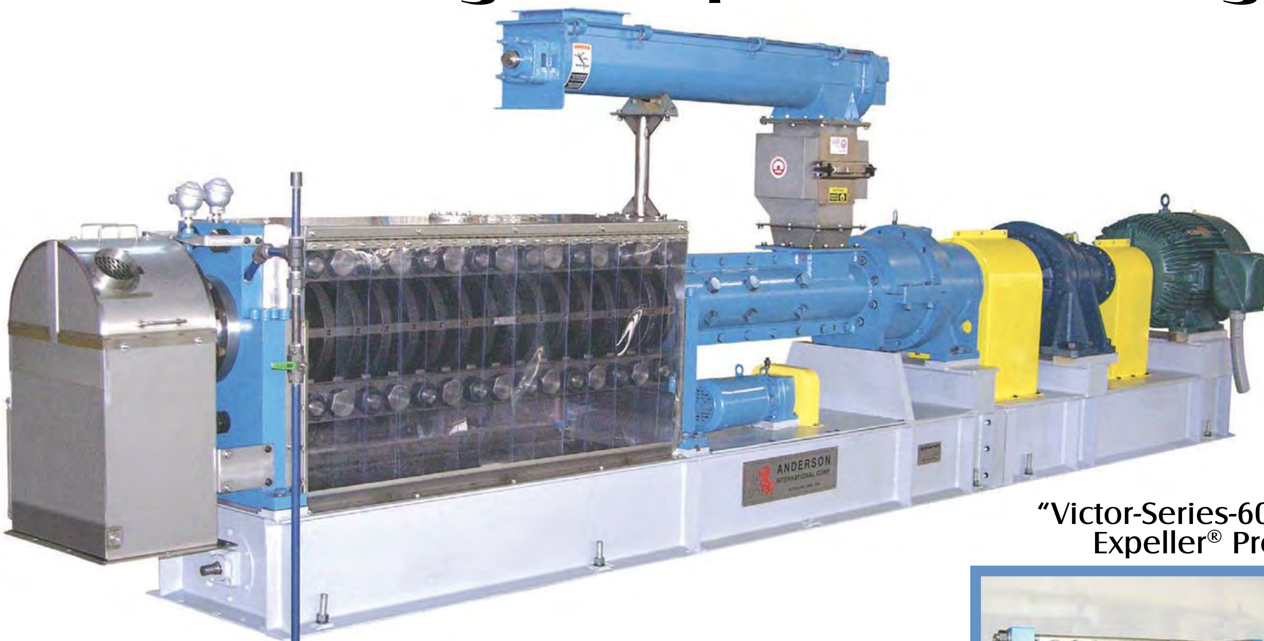

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INFORM

International News on Fats, Oils, and Related Materials

November/December 2013

SUPPLEMENT

AS THE WORLD TURNS . . .

Surfactant suppliers must be agile to meet the needs of their customers whenever and wherever consumer demand takes them.

Tom Branna

Tom Branna is vice president and editorial director for Rodman Media, where he is also editor of Happi *magazine. He can be contacted at tbranna@rodmanmedia.com.*

Reprinted with permission from the September 2013 issue of Happi *magazine.*

Don't be too quick to sign that JV in Jakarta. Maybe that business trip to Chennai can wait as well. Just when multinationals were convinced that the futures of their companies lay in emerging markets, a new study by Bridgewater Associates LP found that, for the first time since 2007, Japan, Europe and the US are contributing more to growth in the $74 trillion global economy than China, India, Brazil and other emerging markets. Bridgewater, an investment firm that manages the world's largest hedge fund, expects developed markets to contribute 60% of the estimated $2.4 trillion in global growth this year.

China is blamed for much of the slowdown in the fortunes of emerging markets. The country is expected to post growth of 7.5% this year, according to government estimates; not bad, but if accurate, it would be the slowest increase in China's economy since 1990. A slowdown in China could cause a domino effect, resulting in lower demand for goods and services from Southeast Asia and Latin America, according to experts. Household and personal product sales are more resilient than other consumer goods categories, and suppliers say the expanding middle class in both regions has provided a lift to sales—but there has been somewhat of a headwind in recent months, say some industry executives.

"Latin America is a strong force that continues to drive the development of the surfactant market. The growth is not as strong as originally projected, but Latin America is still on the upside of the curve," said Bob Bogadek, business creation leader, Americas, Galaxy Surfactants. "As global corporations, Galaxy Surfactants and TRI-K Industries find it extremely important to have dedicated technical and marketing personnel in each territory to help support our customers."

According to Bogadek, there has been an evolution within the Latin American market over the last few years from copying trends to becoming trendsetters around

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the world. Many of the local companies are becoming a significant force in the international field, such as Natura, Boticario, Ebel and Jafra. Customers are hungry for product information and suggestions for new formulations as the region continues to grow. As disposable income increases, the need for new and unique products arises.

Culturally, it has become important to capitalize on the local ingredients found in the Amazon region and surrounding areas. The Latin American people are proud of their heritage and customs, thereby finding a need to incorporate native sustainable resources to use in formulations to create their own identity, said Bogadek. Evonik is focusing on four megatrends:

- Globalization
- Resource Efficiency
- Health
- Nutrition

The first two in particular are intertwined and relate to the bottom line and sustainability of cleaning products in Latin America and Asia, according to David DelGuercio, senior vice president and general manager, global, household care, Evonik Goldschmidt Corporation.

"Major consumer brands recognize this, and want to deal with suppliers that not only have the portfolio they need today, but also those that take a longer view and are planning years down the line in all regions of the world," he explained.

Jeen International continues to expand its global network, according to Carl Cappabianca, general manager.

"This enables us to reach these rapidly growing markets with both specialty and traditional ingredients, including surfactants."

continue to strengthen our position in these mature markets and serve a diversified customer base."

Croda is promoting value-added products to help its North American and European customers make new marketing claims and create high performance products. In the more developed regions of the world, consumers are looking for products with multi-purpose applications, and Croda is able to service these needs through multifunctional and specialty ingredients that offer a noticeable difference, explained Jeffrey Wu, sales development specialist, home care and geo technologies, Croda.

Meanwhile, in Latin America and Asia, the rising affluence of the middle class has driven demand for household cleaning products.

"Our regional sales teams have done an excellent job strengthening Croda's position in these markets, while also providing valuable input on the needs of our customers and the consumers they service," said Wu.

"The R&D team has developed products and formulation support that meets the needs of the consumer in these regions. These have been critical to our success in emerging markets."

Dhaneshwar Patil, business creation leader, Europe for Galaxy Surfactants, noted that there has been a dramatic shift in buying power in Europe, as consumers shift from prestige to masstige products. Still, Europe remains a cornerstone of the industry.

"Surfactants in Europe are one of the largest categories in the cosmetics industry and possibly the strongest market worldwide," said Patil. "Regardless of market fluctuations, surfactants will always be constant."

SURFACTANTS IN EUROPE ARE ONE OF THE LARGEST CATEGORIES IN THE COSMETICS INDUSTRY AND POSSIBLY THE STRONGEST MARKET WORLDWIDE.

For global surfactant industry suppliers, it is imperative to maintain operations in all parts of the globe, for as demand wanes in one region, it waxes in another. Although European and North American customers remain cautious, there has been a noticeable improvement in these mature markets in the past 12 months, especially pertaining to product development mix, according to Brian Chung, business development manager, home and personal care, Solvay Novecare.

"A year ago, the focus was largely on cost reduction and effectiveness, but now the opportunities we see are clearly more growth-driven," he explained. "Solvay has developed a product portfolio that allows our customers to create formulations that meet their performance objectives. We will

According to Dan Beio, vice president, research and development, RITA, the Asian markets are not necessarily driving the newest technologies, but they are making an impact, particularly in "sulfate-free" surfactants, especially amino acid- and sugar-based chemistries.

"These technologies are becoming more affordable, getting very close, on a formula cost per ounce basis, to their sulfated counterparts," said Beio. "This is exciting because the sulfate-free category is the fastest growing segment of the hair care business."

According to Beio, Asia is adding a new dimension to the global surfactant market, due to quality, low-cost surfactants that help many medium- and small-sized companies compete due to these great prices.

Frank Womack, global business director, functional additives, Air Products, noted that Latin America and Asia remain growth markets for surfactants, although the company does anticipate softening in the Asian market. Air Products is establishing supply capabilities and technical support in these regions to support demand, he added.

In Europe, the company's outlook is more restrained.

"We see the European market stagnating and we do not anticipate a good recovery any time soon," said Womack. "North America seems to be recovering economically and finding value in offerings that deliver VOC reduction, solvent replacement and DfE/sustainability."

Timothy J. Roach, global marketing manager, bath and shower, Lubrizol, said that while the global marketplace is still recovering from a slow economy, emerging markets in Latin America and Asia continue to show excellent growth with promise for continued strong performance.

"Understanding regional product trends and market needs is key to delivering exceptional products to these fast growing markets," he said.

There's been growing demand for prestige products in Europe and North America during the past year, according to Cappabianca.

"The uptick in prestige R&D bodes well for growth later this year and next as new product launches hit market," he said. "We're seeing significant interest in both these regions for natural, greener and more sustainable ingredients in all segments including surfactants that are always in the formulation mix; be it prestige or mass market."

WHAT THEY'RE BUYING

Steve Turner, business line director, household care, Evonik Goldschmidt Corporation noted that advanced wetting characteristics are important to hard-surface cleaners, from kitchen and bath products to floor cleaners and auto washes.

"Superior wetting can 'stretch' the performance of cleaning agents while maintaining or improving cleaning power," explained Turner, who also noted that the home care market is expected to grow along with improvements in the housing market. He pointed to US Department of Housing and Urban Development statistics that show in July 2010, sales of single-family houses were 276,000, with a median sales price of $204,000. In May 2013, sales reached 454,000, with a median price of $271,600.

"Year-over-year job growth and permits for new homes is also improving now and all this bodes well for growth in home care cleaning products going forward," Turner told Happi.

Wu said that many customers are looking to formulate better all-purpose cleaners that deliver multiple benefits and faster cleaning.

"This is the largest segment within the hard surface care category and growing in most markets around the world," he explained. As a result, Croda's multifunctional and specialty ingredients that deliver unique consumer benefits or marketing claims are highly sought after by CPG companies.

In personal care, Beio points to growing demand for sulfate-free surfactant technologies in hair care formulas, but they're not always the easiest chemistries to work with, he warned.

"These products are not easy to thicken, are tough to formulate clear products, have different foaming characteristics and don't always have the same "squeaky clean" rinse out, to name a few," said Beio. "But through diligent formulation, we have been able to create products that our customers are very satisfied with."

Growth in hair styling, body washes and shampoos has been fueled by a shift to natural, greener and more sustainable ingredients, due in part, to regulatory pressures for safer surfactants that are free of DEA and MEA, driven primarily by additions to the California Proposition 65 listings, according to Cappabianca.

"At Jeen, we are actively pursuing several liquid alternatives to these traditional, but pressured, chemistries including a range of MIPA-based approaches," he added.

Jeen's development efforts include MIPA-based ingredients as well as expansion of its Jeesperse cold process wax technology which, Cappabianca said, can often reduce the number of surfactants that need to be added to the formulation and allowing production to be done at lower, more energy efficient, temperatures.

According to BASF, product categories that connect with consumer trends have shown the best opportunity for growth—specifically, consumer convenience, and sustainability.

Galaxy Surfactants executives note that Latin American consumers have always been interested in hair care, but the segment is expanding even more thanks to demand from men.

"Recently, Latin men are becoming very aware of their appearance and as local economies improve, the need to have a better personal care regimen is critical to promote a healthier lifestyle," explained Bogadek. "In the past, having personal care products was a status symbol but it is now an everyday item that has become a necessity. As economic purchasing power increases, many people find they can afford the 'me too' items."

In Europe, skin care including mildness for sensitive skin, anti-aging and male grooming have shown great opportunities for growth, according to Patil.

"As society has become more beauty conscious, the need to look and feel good has become ingrained in the culture," he added.

Looking toward the future, mild surfactants seem the most promising. Some of the products that have seen great success are GalSOFT SCG (sodium cocoyl glycinate), GalSOFT SCI (sodium cocoyl isethionate), Galaxy NaCS (sodium cocoyl sarcosinate) and Galaxy NaLS (sodium lauroyl sarcosinate).

THE REGULATORY CLIMATE

When it comes to regulations, the European Union's Registration, Evaluation, Authorization and restriction of Chemicals

(REACH) and California are top of mind for surfactant suppliers.

"Europe has the drive requirements," explained Beio. "We are forecasting continued growth in our sulfate-free surfactant technologies and we see that trend continuing through 2014."

According to Beio, Proposition 65 in California is helping to drive the transition to sulfate-free. Many companies using ethoxylated sulfated surfactants are now looking at warning labels due to the potential 1,4-dioxane content.

"It's impossible logistically to segment out California with a separate formula, so many are reformulating and looking at switching to alternatives to the sulfates, as long as they perform and cost similarly."

Bogadek of Galaxy agreed that 1,4-dioxane has become a major topic of conversation in surfactant circles, noting that there is need for lower parts per million levels to provide safer and purer products. Years ago, Galaxy began the process of using lower ppm levels of 1,4-dioxane with the goal to provide safer solutions. Sourcing issues play an important role in decision-making.

"It is important for us to maintain production by using only natural resources (palm kernel oil), regardless of costs," said Bogadek. "Galaxy is recognized as a supplier to multinational companies because we produce our surfactants from sustainable sources. Many of our products are Ecocert-registered and recognized among other global regulatory agencies."

Increased regulatory pressure continues around the globe, with the common thread being greater finished good safety for end consumers, observed Roach, who added that the onus is on suppliers to produce products that contain the lowest possible levels of dioxane, residuals and other unwanted materials.

Even sodium lauryl sulfate is being viewed in a new light in the public forum, according to Chung of Solvay Novecare.

"We have noticed that the group of consumers concerned about theories that link SLS to nitrosamines has become more polarized, with scientists and researchers on one side and environmental activists groups on the other."

And yet, more industry experts have come to the conclusion that "natural" does not necessarily mean better, Chung said.

"We are very much aware of the increased interest in clinically or dermatologically tested products, and for hypoallergenic formulations," he added. "Solvay has a resolute commitment regarding the safety of our products and we intend to keep working to address our customer demands."

BASF executives note that as a key partner to the home care and I&I as well as personal care industries, it is important that BASF work with regulators and key stakeholders to enable our customers to develop solutions that meet consumer needs.

"At BASF, product safety and stewardship are fundamental principles and are applied across our surfactant portfolio," they said.

IN LATIN AMERICA AND ASIA, THE RISING AFFLUENCE OF THE MIDDLE CLASS HAS DRIVEN DEMAND FOR HOUSEHOLD CLEANING PRODUCTS.

WHAT'S NEW?

As they weave through global regulatory minefields, suppliers are putting more resources on the ground. For example, Air Products continues to expand its innovation pipeline to develop new products that meet market trends and customer needs, according to Womack.

In the industrial and institutional cleaning market, Air Products launched TomaKleen G-12 additive for solvent replacement in response to continued regulatory pressure on volatile organic carbons (VOCs) as well as the desire for multifunctional ingredients.

"Additionally, we launched Tomadol 902 surfactant for the triple benefit of improved cleaning efficacy, cleaning speed and formulation cost, particularly for hard surface applications," he explained.

Tomadol 902 surfactant is designed to provide superior cleaning and degreasing at reduced use levels, particularly compared to NPE surfactants and NPE-alternatives. It is formulated to be highly compatible with other surfactants and solvents, and can replace oxygenated solvents in many formulations. It is effective over a broad range of temperatures, readily biodegradable and has near-zero VOC.

"Tomakleen G-12 solvent replacement additive is designed for formulators seeking alternatives to oxygenated solvents due to increasing regulations, wanting to improve worker safety and desiring to improve the cleaning performance of hard surface cleaners," Womack concluded.

BASF executives say they remain focused on developing solutions that address customers' market needs. Examples include Texapon high active surfactants used in clear and pearlescent shampoos, bath and shower products, and laundry detergents.

Another is Comperlan, a co-surfactant for personal cleansing applications. Comperlan MIPA, for example, is suitable for use in cleansing systems such as shampoos, body washes, shower gels, liquid hand soaps and facial cleansers, according to BASF.

RITA is committed to making the job of formulating products easier for its customers by offering many custom blends that save time and money, according to Beio.

"Our Ritafactants are a formulator's and compounder's dream," said Beio. "Instead of buying, receiving, QC'ing, inventorying, weighing, adding and possibly heating three or four ingredients, we do it all."

Galaxy Surfactants acquired TRI-K Industries in 2009 and expanded product offerings to include natural actives, cosmetic proteins and multifunctional peptides, said Bogadek, who also noted the company's capacity and global footprint expanded as well.

"A new phenoxyethanol plant was built in Jhagadia, India, increasing our capacity to being among the top few manufacturers of phenoxyethanol in the world," he explained.

Galaxy's Patel also pointed out that in 2011, a new surfactant plant was built in Attaka-Suez, Egypt to serve the large demand of Middle East, European and African regions. More recently, during the past two years, offices have been established in Turkey and The Netherlands.

Jeen International's focus on expanding its global distribution network has been a key component of the company's growth and sustained competitiveness, according to Cappabianca.

"We have found, particularly in the emerging markets, that introduction of our Jeesperse cold process wax technology has been gaining significant traction where single vessel, low energy manufacturing is common and time/cost savings can be significant with formulations ranging from traditional shampoos and lotions to body washes and styling products," he said.

New products for home care and new capacity in emerging markets has been a focus of Evonik during the past year, according to Turner, who explained that last year the company launched Rewoquat WE 45, a liquid-at-room- temperature fabric softener, which has been well received in the market.

"We also launched a new silicone surfactant, Rewocare BDS 15, earlier this year which improves wetting and spreading on hard surfaces for the home care market segment," he added.

Additionally, Evonik is expanding its global presence with new plant capacity underway in China and Brazil capable of producing surfactants from renewable resources. The new capacity in Shanghai is due to come on-stream by the end of 2013, and at a new plant in Brazil by 2014.

Solvay continues to focus primarily on innovation and sustainability, as company executives consider sustainable development a fundamental responsibility, according to Chung. In addition, in the past year, Solvay has made strategic investments in Asia, including start of construction on a large-scale alkoxylation facility in Singapore and the acquisition of Sunshield Chemicals in India.

"While we work toward expanding our influence in Asia and Latin America, we continue to support our customers in Europe and North America, investing in new technologies and delivering state-of-the-art performance," said Chung.

Croda launched ModiSurf Lift earlier this year, which makes cleaning faster and easier for consumers. For customers interested in green technologies, Croda launched NatraSense LF-8, a 100% bio-based surfactant, developed for applications that demand a low foaming, green formulation.

"In support of our manufacturing sustainability initiatives, we've completed the construction of a biofermentation plant in the UK that's producing sophorolipids for the home care cleaning market," said Wu. "Most recently, Croda's acquisition of the specialty products business of Arizona Chemical, including a portfolio of class leading oil gelling polymers, is helping Croda offer new delivery systems and product forms to our customers."

Meeting the needs of consumers whenever and wherever needed remains the goal of surfactant suppliers and their customers—whether they're adding capacity in Guangzhou, expanding product portfolios in Portugal or building sales in São Paulo.

NEW SURFACTANTS

Here is a list of new products that were introduced by surfactant suppliers in the past 14 months. To get more information on any of the products detailed below, contact the supplier directly using the information provided.

AIR PRODUCTS

Allentown, PA
Tel: 610-791-4911
Website: www.airproducts.com

Tomakleen G-12
Description: proprietary
Applications: solvent replacement for hard surface cleaners and degreasers
Use levels: dependent on formulation, typically used at 25 wt% of solvent amount as solvent replacement

Tomadol 902
Description: proprietary
Applications: hard surface cleaning and degreasing
Use levels: designed for high performance at low concentration, with goal of 1 wt% or less depending on formulation

CRODA INC.

Edison, NJ
Tel: 732.417.0800
Website: www.croda.com

CONTINUED ON NEXT PAGE

ModiSurf Lift
Description: Ester
Applications: All-purpose cleaners, glass cleaners, floor cleaners, hard surface care
Use levels: 1-3%
Comments: Surface modification additive that makes next time cleaning easier

NatraSense AG-810
Description: Alkyl polyglucoside
Applications: Hard surface care, fabric care, hand washing
Use levels: 1-5%
Comments: Low colored APG that provides excellent detergency and processing benefits in a wide variety of application areas

Coltide Radiance
Description: Quaternized hydrolyzed wheat protein/silicone copolymers
Applications: Fabric care for color protection, fiber protection, and anti-greying
Use levels: 0.25 grams per wash
Comments: Additive for fabric softeners/conditions that provides fiber and color protection

EVONIK GOLDSCHMIDT CORPORATION

Hopewell, VA
Tel: 804 541-8658
Email: dana.nystrand@evonik.com
Website: www.household-care.evonik.com

Rewocare BDS 15
Description: Organo-modified silicone surfactant
Applications: Ideal for rinse aids in automatic-dishwash and other hard-surface kitchen and bath cleaning products.
Use levels: 0.05 to 0.5%
Comments: Even at low use levels and on hydrophobic surfaces, the readily biodegradable Rewocare BDS 15 silicone surfactant can out-wet fatty alcohol ethoxylates and other standard surfactants by a factor of 10 or more.

GALAXY SURFACTANTS, LTD.

Navi Mumbai, India
Tel: +91 22-6513-4444
Email: bob.bogadek@galaxysurfactants.com, Dhaneshwar.Patil@galaxysurfactants.com
Website: www.galaxysurfactants.com

Galsoft SCG
Description: Sodium cocoyl glycinate
Applications: Toiletries, skin care, hair care, baby care
Use levels: 2-10%
Comments: A mild, natural surfactant composed of glycine and fatty acids

GalHueShield HCS
Description: p-Methoxycinnamidopropyl dimethyl behenyl ammonium chloride
Applications: Hair care
Use levels: 0.5-1.5%
Comments: Multi-functional hair color protector from UV-induced damage and applied hair color treatment. Provides superior conditioning properties, enhancing sensorial attributes.

SunBeat
Description: Methoxycinnamidopropyl hydroxysultaine
Applications: Skin care, sun care
Use levels: 7.5-10%
Comments: Patented, water soluble UVB absorber with excellent substantivity to skin and hair.

JEEN INTERNATIONAL CORPORATION

Fairfield, NJ USA
Tel: 973-439-1401
Email: info@jeen.com
Website: www.jeen.com

Jeesperse ICE-T VICL-C-A
INCI: Stearic acid, glycol stearate, stearamide AMP, carbomer, glyceryl stearate, cetyl alcohol
Use Levels: 1.0-10.0%
Applications: Skin care, hair care, sunscreens, color cosmetics and general skin care formulations
Comments: Launched this spring, the Jeesperse ICE-T instant cold emulsion technology includes optimized powders that, when introduced into water at room temperature, rapidly form stable emulsions typically eliminating the need for traditional emulsifiers and allowing the addition of waxes into the system without heating. Benefits include reduced energy costs, time savings, no cool-down and single vessel production. The Jeesperse ICE-T C-PANT is designed specifically to serve as the core, base product for various hair care conditioning, styling, and related formulations.

ICE-T C-PANT
INCI: Hydroxypropyl guar, cetyl alcohol, behentrimonium chloride, stearamidopropyl dimethylamine, stearic alcohol, cetearyl alcohol, polysorbate 60, glyceryl stearate
Use Levels: 1.0-10.0%
Applications: Hair care, conditioners and a range of related general hair care formulations.
Comments: Launched this spring, the Jeesperse ICE-T instant cold emulsion technology includes optimized powders that, when introduced into water at room temperature, rapidly form stable emulsions typically eliminating the need for traditional emulsifiers and allowing the addition of waxes into the system without heating. Benefits include reduced energy costs, time savings, no cool-down and single vessel production. The Jeesperse ICE-T C-PANT is designed specifically to serve as the core, base product for various hair care conditioning, styling and related formulations.

Jeequat NDCS
INCI: Cetyl alcohol, behentrimonium chloride, cocamidopropyl betain, sorbitan laurate
Use Levels: 3.0-7.0%
Applications: Hair conditioners, leave-in products
Comments: Cold-processable, ready-to-use hair care cationic conditioner concentrate, naturally-derived from rapeseed oil, containing behentrimonium chloride. Has a balanced hydrophile/lipophile profile to ensure the highest viscosity and superior conditioning effect at the lowest cost to address a wide range of formulating needs.

LUBRIZOL ADVANCED MATERIALS, INC.

Brecksville, OH
Tel: 800-379-5389
Email: personalcare@lubrizol.com
Website: www.lubrizol.com/personalcare

Sulfochem ES-70DXS Surfactant

Description: Sodium laureth (2) sulfate
Applications: Personal and household cleansing products.
Use levels: As-supplied, when used as a primary surfactant, the recommended use level for personal care applications is 10-40 wt% and 5-30 wt% for home care applications.
Comments: This vegetable-based, highly flowable, easy-to-process surfactant is supplied as a highly concentrated product (70% active). In surfactant cleansing formulations, it exhibits excellent flash foaming properties and has very low residual color and odor. It contains less than 10 ppm residual 1,4-dioxane and is antioxidant and preservative-free.

Sulfochem ES-70US Surfactant

Description: Sodium laureth (2) sulfate
Applications: Personal and household cleansing products.
Use levels: As-supplied, when used as a primary surfactant, the recommended use level for personal care applications is 10-40 wt% and 5-30 wt% for home care applications.
Comments: This vegetable-based, highly flowable, easy-to-process surfactant is supplied as a highly concentrated product (70% active). In surfactant cleansing formulations, it exhibits excellent flash foaming properties and has very low residual color and odor and it is anti-oxidant and preservative-free.

RITA CORPORATION

Crystal Lake, IL
Tel: 815-337-2500
Email: sales@ritacorp.com
Website: www.ritacorp.com

Ritafactant 138ANLG

Description: Decyl glucoside, lauryl glucoside, sodium lauroyl lactylate
Applications: Foaming agent used in shampoos, liquid hand cleansers, body wash, facial cleanser Use levels: 5-30%
Comments: This patented, very mild and high foaming combination of sugar based glucosides and lactylates gently cleans without stripping away epidermal and inter-cuticle skin and hair lipids. The lactylate, being an "interrupted soap" acts as a cleanser, and emulsifier, and leaves a very nice skin after feel. We have taken on the difficulty of melting and handling the lactylate into a blend of sulfate-free surfactants so our customers can add this cold to any formulation.

Ritafactant SCI-2

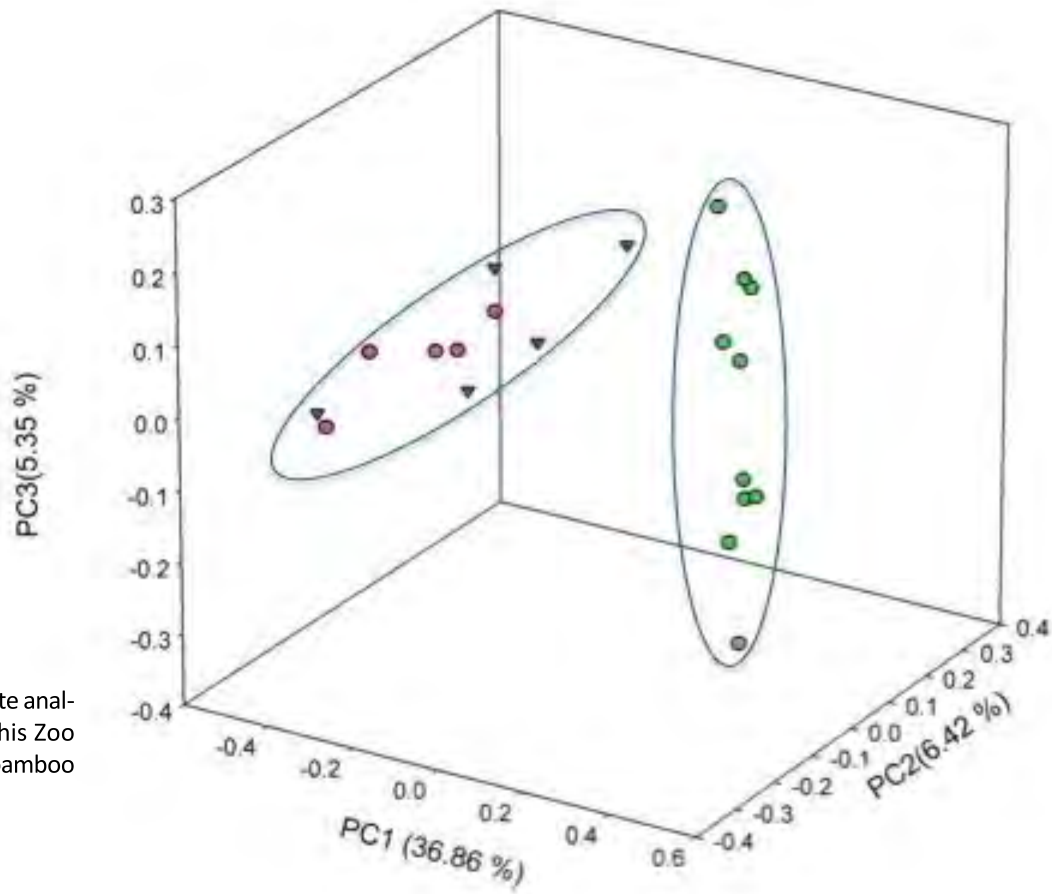
Description: Cocamidopropyl betaine and sodium cocoyl isethionate
Applications: Foaming agent used in shampoos, liquid hand cleansers, body wash, facial cleanser
Use levels: 5-15%
Comments: This combination of sulfate free surfactants provide very high foaming and give the foam that is produced a very creamy feel. This combination can be used as the primary foaming contributor or can be used as secondary foamer, since it creates mounds of "flash" foam. We have taken on the difficulty of melting and handling the Isothionate into this blend of betaine so our customers can add this cold to any formulation.

Ritathix DOE

Description: PEG-120 methyl glucose dioleate and methyl gluceth-10
Applications: Thickener used in all types of surfactant systems
Use levels: 0.5-2.5%
Comments: This unique combination of thickening ingredient and solvent allows us to create a liquid thickener which works perfectly with sulfate free surfactants, which are very difficult to thicken. You can also create crystal clear formulations using this thickener. And, unlike other PEG thickeners, you don't get that "plastic" structure. It creates more of a Newtonian gel structure, which allows for even very thick liquids to disperse more readily onto the hair, resulting is much less frictional stress being placed on the wet hair.

S10

FIGURE FROM PAGE 632 SHOWING THE BASELINE FOR THE GIANT PANDA GUT MICROBIOME



Unweighted principal coordinate analysis of microbes from Memphis Zoo (▲) Male, (●) Female and (●) bamboo (leaf and culm of five species).

EXTRACTS & DISTILLATES

Short-term and long-term effects of excessive consumption of saturated fats and/or sucrose on metabolic variables in Sprague Dawley rats: a pilot study

Pranprawit, A., *et al.*, *J. Sci. Food Agric. 93*:3191–3197, 2013.

Feeding high-fat and/or high-sugar diets to rats leads to a change in markers of metabolic syndrome. However, types and amounts of fat and sugar as well as the length of the experiment for establishing diet-induced metabolic syndrome in the Sprague-Dawley (SD) rat model remain uncertain. This study was designed to investigate the effects in SD rats of consuming excess lard, sucrose, or a combination of lard and sucrose for a short (4 week) or long (8 week) period of time. Consumption of the high-fat high-sugar (HFHS) diet significantly increased weight gain and abdominal fat weights ($P < 0.05$), and the rats also began to develop signs of impaired glucose tolerance and had increased fasting blood lipids glucose and insulin concentrations. The high-fat (HF) diet mainly affected weight gain and fat deposition, whereas the high-sugar (HS) diet induced glucose intolerance but not the obesity-related parameters. Control rats showed a tendency toward insulin resistance and glucose intolerance when fed for a long-term period. The lard plus sucrose-based HFHS diet is the most efficient one for inducing signs of metabolic syndrome, and SD rats fed this diet for 8 weeks successfully develop obesity and insulin resistance, which can be used as a model for metabolic syndrome research.

Omega-3 long-chain polyunsaturated fatty acid enriched eggs by microalgal supplementation

Lemahieu, C., *et al.*, *Lipid Technol. 25*:204–206, 2013.

The health-promoting effects of omega-3 polyunsaturated fatty acids (n-3 PUFA) are mainly ascribed to the n-3 long-chain (LC)-PUFA, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). However, their intake is mostly below the recommended daily intake. A possible way to raise their average intake is to enrich food products with n-3 LC-PUFA. Addition of autotrophic microalgae to the diet of laying hens can increase the level of these fatty acids in the egg yolk. Moreover, depending on the microalgal species, other nutritionally interesting algal carotenoids can also be transferred to the egg yolk. As a consequence, egg yolk color changes may occur. A survey conducted among 511 people showed that they will buy n-3 PUFA-enriched products, such as enriched eggs, and are even prepared to pay more for these products. However, the change of the yolk color must be taken into account, since consumer acceptability decreases when a deeply red yolk color is obtained.

Plasma lipid profiling in a large population-based cohort

Weir, J.M., *et al.*, *J. Lipid Res. 54*:2898–2908, 2013.

We have performed plasma lipid profiling using liquid chromatography electrospray ionization tandem mass spectrometry on a population cohort of more than 1,000 individuals. From 10 μL of plasma we were able to acquire comparative measures of 312 lipids across 23 lipid classes and subclasses including sphingolipids, phospholipids, glycerolipids, and cholesterol esters (CE) in 20 min. Using linear and logistic regression, we identified statistically significant associations of lipid classes, subclasses, and individual lipid species with anthropometric and physiological measures. In addition to the expected associations of CE and triacylglycerol with age, sex, and body mass index (BMI), ceramide was significantly higher in males and was independently associated with age and BMI. Associations were also observed for sphingomyelin with age, but this lipid subclass was lower in males. Lysophospholipids were associated with age and higher in males but showed a strong negative association with BMI. Many of these lipids have previously been associated with chronic diseases including cardiovascular disease and may mediate the interactions of age, sex, and obesity with disease risk.

Inhibitory effects of different forms of tocopherols, tocopherol phosphates, and tocopherol quinones on growth of colon cancer cells

Dolfi, S.C., *et al.*, *J. Agric. Food Chem. 61*:8533–8540, 2013.

Tocopherols are the major source of dietary vitamin E. In this study, the growth inhibitory effects of different forms of tocopherols (T), tocopheryl phosphates (TP), and tocopherol quinones (TQ) on human colon cancer HCT116 and HT29 cells were investigated. δ-T was more active than γ-T in inhibiting colon cancer cell growth, decreasing cancer cell colony formation, and inducing apoptosis; however, α-T was rather ineffective. Similarly, the rate of cellular uptake also followed the ranking order δ-T > γ-T ≥> α-T. TP and TQ generally had higher inhibitory activities than their parent compounds. Interestingly, the γ forms of TP and TQ were more active than the δ forms in inhibiting cancer cell growth, whereas the α forms were the least effective. The potencies of γ-TQ and δ-TQ (showing

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IC_{50} values of ~0.8 and ~2 μM on HCT116 cells after a 72 h incubation, respectively) were greater than 100-fold and greater than 20-fold higher, respectively, than those of their parent tocopherols. Induction of cancer cell apoptosis by δ-T, γ-TP, and γ-TQ was characterized by the cleavage of caspase 3 and PARP1 [poly (ADP-ribose) polymerase 1] and DNA fragmentation. These studies demonstrated the higher growth-inhibitory activity of δ-T than γ-T, the even higher activities of the γ forms of TP and TQ, and the ineffectiveness of the α forms of tocopherol and their metabolites against colon cancer cells.

Docosahexaenoic acid from algal oil

Kuratko, C.N., and N. Salem, Jr., *Eur. J. Lipid Sci.Technol. 115*:965–976, 2013.

Certain algae produce long-chain omega-3 fatty acids including eicosapentaenoic (EPA) and docosahexaenoic (DHA) acids as part of normal metabolism. In nature, these fatty acids enter the food chain and are important nutrients for the health of many animals, including humans. Cultured under specific and tightly controlled conditions, these algae synthesize oils that are commercially produced for use in infant formula, foods, beverages, and a variety of supplements. EPA and DHA have long been associated with cardiovascular health. More recently the impact of DHA, as the primary n-3 fatty acid in brain and retinal tissue, has been documented. Within membranes, DHA facilitates cell signaling and serves as a precursor to highly bioactive molecules. Because endogenous production is low, levels of DHA in brain, retina, and other tissues do not reach higher levels unless this preformed fatty acid is included in the diet. Most Westernized diets provide low levels of EPA and DHA, making their use in supplements and fortified foods necessary for optimal health.

Influence of free fatty acids on oxidative stability in water-in-walnut oil emulsions

Yi, J., *et al.*, *Eur. J. Lipid Sci. Technol. 115*:1013–1020, 2013.

The effect of free fatty acids (FFA) on lipid oxidation in water-in-stripped walnut oil emulsions was investigated. The formation of the primary oxidation products (hydroperoxides) and the secondary oxidation product (headspace hexanal) increased with increasing addition of oleic acid to the emulsions. However, oleic acid at high concentrations was primarily involved in accelerating hydroperoxide formation at early stage and then hydroperoxide decomposition rapidly after hydroperoxides reached the maximum point. The prooxidant effect of saturated FFA was dependent on their chain length with lipid oxidation rates being in the order of lauric acid > palmitic acid > stearic acid. The highest prooxidant activity of lauric acid among these FFA was probably due to its largest polarity and making the water droplet interface more negatively charged than the others when the aqueous phase pH was 7.0, which was above its pK_a, thereby attracting prooxidant metals to the water droplet surface. The highest ability to promote lipid oxidation in water-in-oil emulsions was shown by linolenic acid, followed by linoleic and oleic acids, indicating that the oxidative capacity increased with increasing degree of unsaturation. The prooxidant effect of FFA with the *cis* double bonds was lower than those with the *trans* ones when oleic acid (18:1, *cis*) was compared to elaidic acid (18:1, *trans*) and linoleic acid (18:2, *cis-cis*) was compared to linoelaidic acid (18:2, *trans-trans*), which suggested that geometric isomerization of FFA influenced lipid oxidation rates of water-in-oil emulsions.

Comparative study of two methods (hexane extraction and NMR) for the determination of oil content in an individual olive fruit

Deblangey, A., *et al.*, *Eur. J. Lipid Sci. Technol. 115*:1070–1077, 2013.

The performance of NMR spectroscopy and hexane/isopropanol extraction (HIE) for the determination of oil content in individual olive fruit has been investigated. Both analytical methods, which are based on conventional protocols, have been adapted for samples consisting of unground pulp shreds obtained from a single olive fruit. NMR offers better precision than HIE. The latter generates more result errors during two critical steps of the protocol: weighing and lipid phase recovery. Significant differences were observed between both methods when applied on the same samples. A bias and a slope factor were highlighted, and these resulted from extraction efficiency issues related to the specific structure of the sample. HIE gives results that are closer to the reference method (i.e., Soxhlet extraction) than NMR. Thus, (i) the determination of oil content in a single olive is feasible; (ii) given that NMR is faster, requires less sample handling, and is less sensitive to the structure of samples, it was considered as the more suitable of the two techniques for routine measurements of oil content in individual olive fruit.

Interaction of organic solvents with the epicuticular wax layer of wheat leaves

Myung, K., *et al.*, *J. Agric. Food Chem. 61*:8737–8742, 2013.

After foliar application, compounds that are not absorbed into leaves can be removed from the leaf surface by dipping or rinsing in dilutions of organic solvents in water. However, interactions between solvent mixtures and the epicuticular wax layer have received little attention, and information on potential physical and chemical intactness of the plant surface following application of solvents is limited. In this study, wheat leaves were dipped in organic solvents at different dilutions with water, and the major component of the leaf epicuticular wax layer, 1-octacosanol, was analyzed to assess damage to the wax layer. Dipping leaves in dilutions of organic solvent higher than 60% by volume resulted in only negligible or low levels of 1-octacosanol extraction, while no 1-octacosanol was detected in any mixtures containing less than 40% organic solvent.

Furthermore, analysis of leaf surfaces by scanning electron microscopy showed structural intactness of the epicuticular wax layer when organic solvent mixtures were used. Therefore, our results demonstrate that the epicuticular wax layer of wheat leaves is not altered physically or chemically by organic solvent solutions up to 40% by volume. These findings validate the use of solvent washing procedures to assess unabsorbed compounds on wheat leaf surfaces.

Synthesis of phytosteryl ester containing pinolenic acid in a solvent-free system using immobilized *Candida rugosa* lipase

No, D.S., *et al.*, *J. Agric. Food Chem. 61*:8934–8940, 2013.

Phytosteryl ester synthesized with pinolenic acid (PLA) from pine nut oil is expected to have features of both phytosterol and PLA. In this study, lipase from *Candida rugosa* (CRL) was immobilized and then used to optimize conditions for synthesis of phytosteryl ester containing PLA. Lewatit VP OC 1600, a macroporous hydrophobic resin, was selected as the best carrier, and the optimum condition for the immobilization of CRL was established. With immobilized CRL prepared, synthesis of phytosteryl ester with fatty acid from pine nut oil was carried out. Parameters investigated were temperature, molar ratio (phytosterol to fatty acid), enzyme loading, and vacuum. Optimum conditions for synthesis of phytosteryl ester were a temperature of 60°C, molar ratio of 1:4, enzyme loading of 10% (based on the total weight of the substrate), and pressure of 80 kPa. The maximum conversion of phytosteryl ester was *ca.* 93 mol% at the optimum condition.

Identification of cholesteryl ester of ferulic acid in human plasma by mass spectrometry

Nagy, K., *et al.*, *J. Chromatogr. A 1301*:162–168, 2013.

Epidemiological data suggest that regular consumption polyphenol-rich foods and beverages is associated with a reduced risk of certain pathological conditions. While the *in vivo* "per se" antioxidant benefit of polyphenols still has not been clearly demonstrated, it has been suggested that phenolic acids can be incorporated into low-density lipoproteins. In the present study, we hypothesized that esterification of phenolic acids such as ferulic acid with lipophilic substances such as cholesterol can occur *in vivo*. To prove this hypothesis, we have synthesized pure cholesteryl ferulate standard and used gas and liquid chromatography coupled with mass spectrometry to confirm the presence of endogenous form in human plasma. The detection and identification of cholesteryl ferulate was based on: (i) matching gas and liquid chromatographic retention times with the reference standard, (ii) accurate mass of the molecular ion, (iii) matching electron ionization mass spectrum, and (iv) matching electrospray product ion spectrum. The identified cholesteryl ferulate demonstrated an *in vitro* antioxidant capacity in various assays. The present study confirmed that phenolic acid can be found in human plasma as lipophilic conjugates that exert antioxidant capacity. These molecules can potentially be involved in the protection of lipoproteins against oxidative damages.

Enrichment and quantification of monoacylglycerols and free fatty acids by solid phase extraction and liquid chromatography–mass spectrometry

Chu, B.S., and K. Nagy, *J. Chromatogr. B 932*:50–58, 2013.

Quantification of monoacylglycerols (MAG) and free fatty acids (FA) is of interest in biological systems and in food, cosmetic, and pharmaceutical products. This manuscript describes and validates a reversed-phase liquid chromatography–tandem mass spectrometry-based approach for simultaneous quantification of these analytes in fats and oils. Purification and concentration of MAG/FA were performed using cation exchange solid phase extraction, which allowed elimination of the abundant triacylglycerols. Following cleanup and concentration, the analytes were separated and detected with the aid of volatile ammonium-formate buffer. MAG were detected in positive ion mode, while FA were detected in negative ion mode. The method was validated by the method of standard additions and by using stable isotope-labeled internal standards. The results confirm the feasibility of quantifying these two classes of analytes simultaneously without any chemical derivatization. The obtained main quantitative features include: (i) lower limits of quantification: 1–30 ppm for MAG analytes, (ii) lower limits of quantification: 90–300 ppm for FA analytes, (iii) averaged interbatch precision: 6%, and (iv) averaged bias: –0.2% for MAG and 0.5% for FA. Various animal fat and vegetable oil samples were characterized for their MAG/FA profile indicating the usefulness of the method to address quality and authenticity of fats and oils.

On the glucoside analysis: Simultaneous determination of free and esterified steryl glucosides in olive oil. Detailed analysis of standards as compulsory first step

Gómez-Coca, R.B., *et al.*, *Food Chem. 141*:1273–1280, 2013.

This work covers two important gaps in the field of micronutrient databases: Herein we describe a short and easy protocol that allows the analysis of both free and esterified steryl glucosides in olive oil. By utilizing accurate quantitative

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methods, we achieve a better understanding of olive oil composition and health-promoting properties. The procedure consists of isolating the fraction of interest through solid-phase extraction and using gas chromatography–flame ionization detection for both identification and quantification of the derivatized species. Additionally, mass spectrometry detection has been utilized for confirming the identity of the individual esterified steryl glucosides in some cases. The method's limit of detection has been set at 0.37 mg/kg for each free steryl glucoside and 0.20 mg/kg for each esterified steryl glucoside, whereas the recoveries are around 96% and 77%, respectively. Finally, we provide a complete analysis of the commercial standard for esterified steryl glucosides, since such information was not yet available.

Analysis of wax esters by silver-ion high-performance liquid chromatography–tandem mass spectrometry

Vrkoslav, V., *et al.*, *J. Chromatogr. A 1302*:105–110, 2013.

Wax esters (WE), esters of long-chain fatty acids and long-chain alcohols, were analyzed by Ag-HPLC/APCI-MS/MS [silver ion high-performance liquid chromatography/atmospheric pressure chemical ionization–tandem mass spectroscopy]. Two ChromSpher Lipids columns connected in series (a total length of 50 cm) and hexane/2-propanol/acetonitrile mobile phases were used to achieve good separation of the molecular species. The chromatographic behavior of WE was studied under optimized conditions: Retention increased with the number of double bonds and with the temperature (15–35°C); retention times were affected by the double-bond position, *trans* isomers eluted earlier than *cis* isomers, and the WE were partially separated depending on the aliphatic-chain length. The WE provided simple APCI spectra with $[M+H]^+$ ions; the MS/MS spectra showed fragments, which allowed their identification. The method was applied for an analysis of the WE mixtures from jojoba oil and human hair, and the results were compared with analogous data from an optimized reversed phase-HPLC system.

Generating omega-3 rich olive oil by cross breeding

Ozdemir, Y., *et al.*, *Eur. J. Lipid Sci. Technol. 115*:977–981, 2013.

In this research, 14 hybrid table olive genotypes were used as material that was harvested from Olive Breeding Parcels in Atatürk Central Horticultural Research Institute (Yalova, Turkey), and their maturation index, oil content, fatty acid composition, and omega-6/omega-3 fatty acid ratio were evaluated. These genotypes were generated by crossing Gemlik, Manzanilla, Ascolana, Edinciksu, Uslu, and Tavşan yüreği olive cultivars during cross breeding studies of a national project. Oil was obtained from fruit of olive genotypes by cold pressing. Maturation index and oil content of genotypes were determined between 2.6–6.4 and 22.43–28.12 (%), respectively. Linolenic acid distributions in fatty acid composition of genotype's oil were detected between 0.5–1.33 (% in fatty acids). Some olive genotypes' oils had high linolenic characteristics that have potential for supporting the necessary intake of omega-3. Also, some of them had desirable omega-6/omega-3 fatty acid ratios, which were between 3.74 and 4.00.

LipidBlast *in silico* tandem mass spectrometry database for lipid identification

Kind, T., *et al.*, *Nat. Methods 10*:755–758, 2013.

Current tandem mass spectral libraries for lipid annotations in metabolomics are limited in size and diversity. We provide a freely available computer-generated tandem mass spectral library of 212,516 spectra covering 119,200 compounds from 26 lipid compound classes, including phospholipids, glycerolipids, bacterial lipoglycans, and plant glycolipids. We show platform independence by using tandem mass spectra from 40 different mass spectrometer types including low-resolution and high-resolution instruments.

Role of ceramide in diabetes mellitus: evidence and mechanisms

Galadari, S., *et al.*, *Lipids Health Disease 12*: 98, 2013.

Diabetes mellitus is a metabolic disease with multiple complications that causes serious diseases over the years. The condition leads to severe economic consequences and is reaching pandemic level globally. Much research is being carried out to address this disease and its underlying molecular mechanism. This review focuses on the diverse role and mechanism of ceramide, a prime sphingolipid signaling molecule, in the pathogenesis of type 1 and type 2 diabetes and its complications. Studies using cultured cells, animal models, and human subjects demonstrate that ceramide is a key player in the induction of β-cell apoptosis, insulin resistance, and reduction of insulin gene expression. Ceramide induces β-cell apoptosis by multiple mechanisms, namely, activation of extrinsic apoptotic pathway, increase in cytochrome c release, free radical generation, induction of endoplasmic reticulum stress, and inhibition of Akt [protein kinase B]. Ceramide also modulates many of the insulin signaling intermediates such as insulin receptor substrate, Akt, and Glut-4; and it causes insulin resistance. Ceramide reduces the synthesis of insulin hormone by attenuation of insulin gene expression. Better understanding of this area will increase our understanding of the contribution of ceramide to the pathogenesis of diabetes and further help in identifying potential therapeutic targets for the management of diabetes mellitus and its complications.

Phosphoinositides: tiny lipids with giant impact on cell regulation

Balla, T., *Physiol. Rev. 93*:1019–1137, 2013.

Phosphoinositides (PI) make up only a small fraction of cellular phospholipids, yet they control almost all aspects of a cell's life and death. These lipids gained tremendous research interest as plasma membrane signaling molecules when discovered in the 1970s and 1980s. Research in the last 15 years has added a wide range of biological processes regulated by PI, turning these lipids into one of the most universal signaling entities in eukaryotic cells. PI control organelle biology by regulating vesicular trafficking, but they also modulate lipid distribution and metabolism via their close relationship with lipid transfer proteins. PI regulate ion channels, pumps, and transporters and control both endocytic and exocytic processes. The nuclear PI have grown from being an epiphenomenon to a research area of their own. As expected from such pleiotropic regulators, derangements of PI metabolism are responsible for a number of human diseases ranging from rare genetic disorders to the most common ones such as cancer, obesity, and diabetes. Moreover, it is increasingly evident that a number of infectious agents hijack the PI regulatory systems of host cells for their intracellular movements, replication, and assembly. As a result, PI-converting enzymes began to be noticed by pharmaceutical companies as potential therapeutic targets. This review is an attempt to give an overview of this enormous research field focusing on major developments in diverse areas of basic science linked to cellular physiology and disease.

Organellar lipidomics—background and perspectives

Klose, C., *et al.*, *Curr. Opin. Cell Biol.* *25*:406–413, 2013.

The basic structural units of eukaryotic cells are membrane-bound organelles, and many essential cellular processes take place in and on membranes. It is becoming increasingly clear that these processes are influenced by the biophysical properties of the organelle membranes, which in turn are affected by their lipid composition. Even subtle changes in lipid composition can have a tremendous impact on membrane properties and the processes occurring within them. Therefore, to understand the contribution of membrane lipid composition to the functionality of membrane-bound cellular processes, comprehensive structural and quantitative information on the organellar lipidome is essential. Here we argue that only mass spectrometry-based organellar lipidomics can provide this information today.

Plasma lipidomic profile signature of hypertension in Mexican American families: specific role of diacylglycerols

Kulkarni, H., *et al.*, *Hypertension* *62*:621–626, 2013.

Both as a component of metabolic syndrome and as an independent entity, hypertension poses a continued challenge with regard to its diagnosis, pathogenesis, and treatment. Previous studies have documented connections between hypertension and indicators of lipid metabolism. Novel technologies, such as plasma lipidomic profiling, promise a better understanding of disorders in which there is a derangement of lipid metabolism. However, association of plasma lipidomic profiles with hypertension in a high-risk population, such as Mexican Americans, has not been evaluated before. Using the rich data and sample resource from the ongoing San Antonio Family Heart Study, we conducted plasma lipidomic profiling by combining high-performance liquid chromatography with tandem mass spectroscopy to characterize 319 lipid species in 1,192 individuals from 42 large and extended Mexican American families. Robust statistical analyses using polygenic regression models, liability threshold models, and bivariate trait analyses implemented in the SOLAR software were conducted after accounting for obesity, insulin resistance, and relative abundance of various lipoprotein fractions. Diacylglycerols (DG) in general and the DG 16:0/22:5 and DG 16:0/22:6 lipid species in particular were significantly associated with systolic blood pressure, diastolic blood pressure, and mean arterial pressure, as well as liability of incident hypertension measured during 7,140.17 person-years of followup. Four lipid species, including the DG 16:0/22:5 and DG 16:0/22:6 species, showed significant genetic correlations with the liability of hypertension in bivariate trait analyses. Our results demonstrate the value of plasma lipidomic profiling in the context of hypertension and identify disturbance of DG metabolism as an independent biomarker of hypertension.

Role of omega-3 fatty acids in obesity, metabolic syndrome, and cardiovascular diseases: a review of the evidence

Lorente-Cebrian, S., *et al.*, *J. Physiol. Biochem.* *69*:633–651, 2013.

The present review aims to illustrate current knowledge about the efficacy of omega-3 long-chain polyunsaturated fatty acids (n-3 LC-PUFA) in treating/preventing several metabolic pathologies. We reviewed systematically the published evidence on the effectiveness of n-3 LC-PUFA fish consumption or n-3 LC-PUFA supplementation on prevention/treatment of obesity, metabolic syndrome, and cardiovascular diseases. Most of the reviewed studies were randomized-controlled interventional trials, although some relevant prospective and cross-sectional studies as well as some meta-analyses were also reviewed. Supplementation with n-3 LC-PUFA might improve some obesity-associated metabolic syndrome features such as insulin resistance, hypertension, and dyslipidemia by decreasing plasma triglycerides. Moreover, the blood pressure-lowering and anti-inflammatory properties of these fatty acids and their benefits in vascular function might confer cardioprotection. However, the efficacy of n-3 LC-PUFA on reducing myocardial infarction, arrhythmia, cardiac and sudden death, or stroke is controversial. Due to the beneficial actions of n-3 LC-PUFA, several worldwide government and health organizations have established some recommendations of n-3 LC-PUFA intake for groups of population. In general, the recommended levels for diseases prevention are lower than those advised for particular treatments. However, more clinical trials are necessary to recommend the most effective dosages and formulas (type of n-3

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STATISTICAL ANALYSIS FROM MINTEC

Yuliya Nam-Wright at Mintec

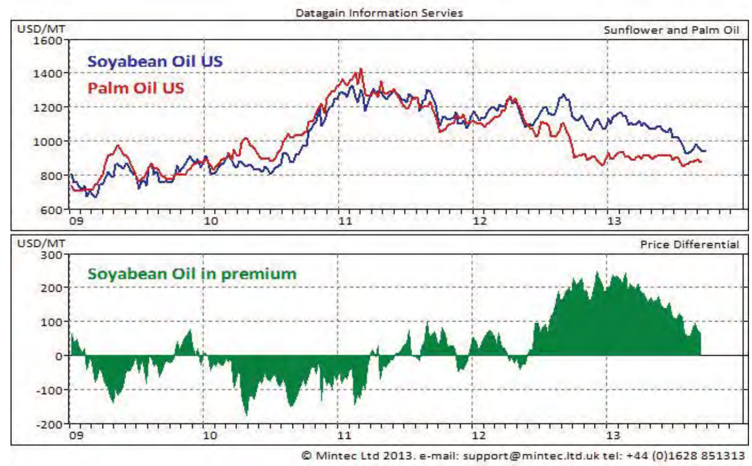
Mintec

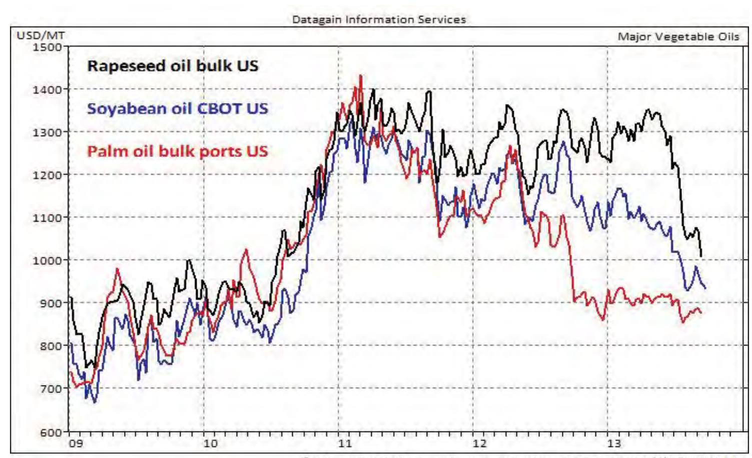
Oils and fats are one of the many markets that have been experiencing a general downward trend. Prospects of higher global production of soybeans following last year's record crop have helped to support their downward price slide. World production of soybeans is forecast at 281.7 million metric tons (MMT) in 2013/14, up 5% year-on-year. Soybean crush is expected to grow slower, by 4%, to 237.9 MMT, and consumption of soybean oil is expected to rise 4% to 44.3 MMT. Ending stocks of soybeans are forecast to increase 16% to 72.3 MMT.

Palm oil prices have fared better than most other oils in the first half of the year as demand was boosted by its attractive price positioning. However, prices have weakened in recent months. World production is forecast to reach a new record high of 58.1 MMT in 2013/14, up 5% year-on-year; and ending stocks are expected to rise by 21% to 9.7 MMT in 2013/14.

Global production of sunflower seed is forecast to rise to a record high of 41.8 MMT in 2013/14, up 15% on last season's drought-affected crop. Crush is expected to rise 10% to 40.7 MMT, and production of sunflower oil is forecast to rise 10% to 15.4 MMT.

World production of rapeseed is forecast to rise 7% year-on-year to 66.4 MMT, driven by higher supplies from all major producing regions. A record crop is expected from Canada, and if current forecasts are realized, Europe will produce the third-largest crop ever produced. Rapeseed crush is forecast to remain largely unchanged at around 62.5 MMT.





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LC-PUFA, eicosapentaenoic acid/docosahexaenoic acid ratio) for specific pathologies.

The role of phospholipids in the biological activity and structure of the endoplasmic reticulum

Lagace, T.A., and N.C. Ridgway, *Biochim. Biophys. Acta 1833*:2499–2510, 2013.

The endoplasmic reticulum (ER) is an interconnected network of tubular and planar membranes that supports the synthesis and export of proteins, carbohydrates, and lipids. Phospholipids, in particular phosphatidylcholine (PC), are synthesized in the ER where they have essential functions including provision of membranes required for protein synthesis and export, cholesterol homeostasis, and triacylglycerol storage and secretion. Coordination of these biological processes is essential, as highlighted by findings that link phospholipid metabolism in the ER with perturbations in lipid storage/secretion and stress responses, ultimately contributing to obesity/diabetes, atherosclerosis, and neurological disorders. Phospholipid synthesis is not uniformly distributed in the ER but is localized at membrane interfaces or contact zones with other organelles, and in dynamic, proliferating ER membranes. The topology of phospholipid synthesis is an important consideration when establishing the etiology of diseases that arise from ER dysfunction. This review will highlight our current understanding of the contribution of phospholipid synthesis to proper ER function, and how alterations contribute to aberrant stress responses and disease. ■