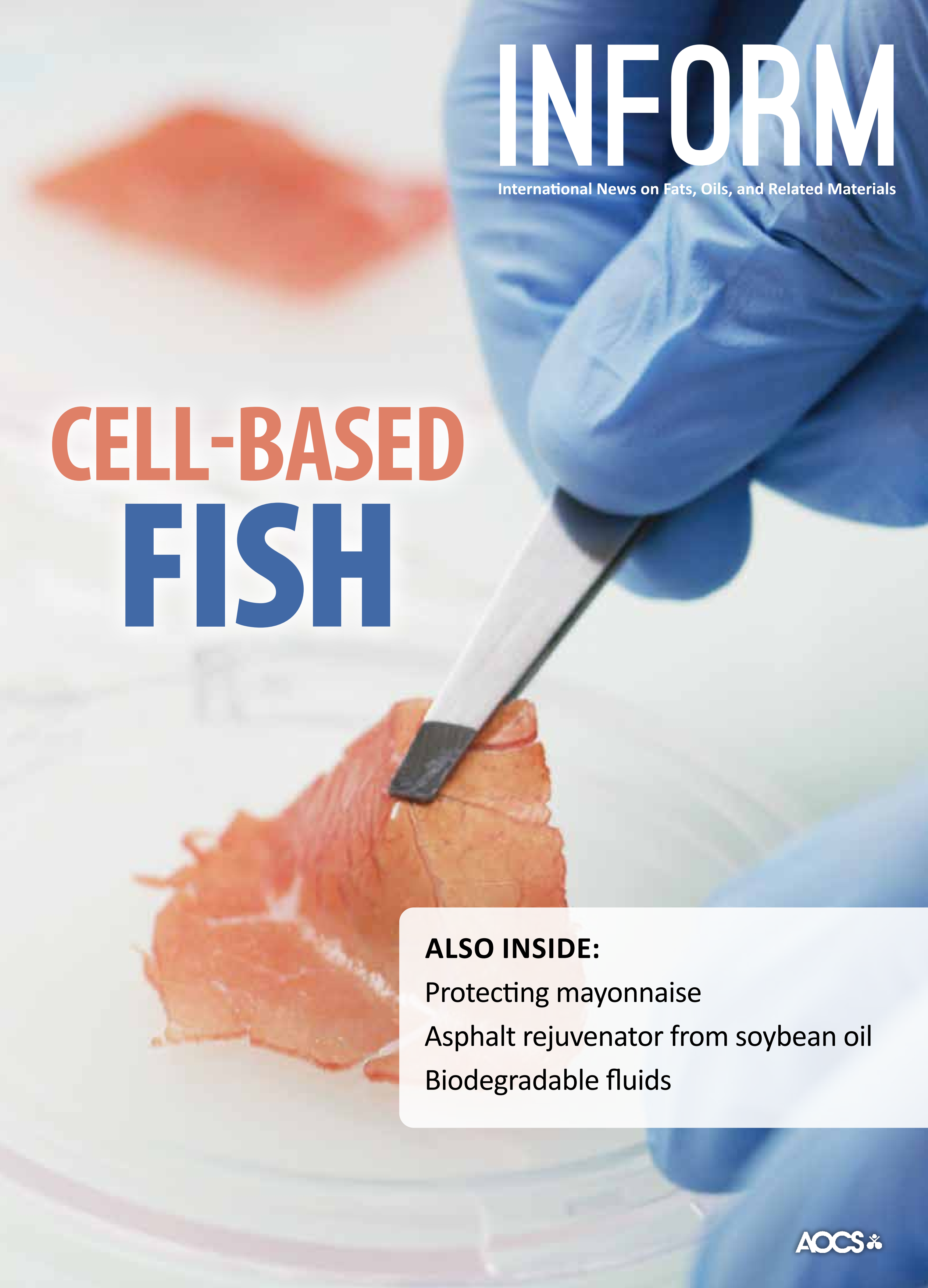
INFORM June 2021 Volume 32 (6)



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CONTENTS

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INFORM
International News on Fats, Oils, and Related Materials
ISSN: 1528-9303 IFRMEC 32 (6)

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Inform (ISSN: 1528-9303) is published 10 times per year in January, February, March, April, May, June, July/August, September, October, November/December by AOCS Press, 2710 South Boulder Drive, Urbana, IL 61802-6996 USA. Phone: +1 217-359-2344. Periodicals Postage paid at Urbana, IL, and additional mailing offices. **POSTMASTER:** Send address changes to *Inform*, P.O. Box 17190, Urbana, IL 61803-7190 USA.

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Poisson from a petri dish

Rebecca Guenard

Our oceans are in trouble. According to a report released by the United Nations Food and Agriculture Organization (FAO) last summer, the percentage of the world's marine fisheries classified as overfished has increased continuously from 10% in 1975 to 34.2% in 2017. Fish consumption exceeds all other animal proteins eaten per capita worldwide and increases at an average rate of 3.1% per year. High demand results in overfishing which depletes stock faster than they replenish, lowering populations and threating future production. The report indicates that the problem is particularly acute in developing nations where unstructured governments execute limited management (https://doi.org/10.4060/ca9229en).

- **Making cell-based seafood is technically complicated and extremely expensive, but a select group of companies driven by a conviction that it will provide sustainability and food security for future generations are taking on the challenge.**
- **Regulators in some parts of the world have given the cultured meats industry a green light. How will other countries regulate these products?**
- **Projections indicate cellular agriculture could become mainstream in the next decade. What will that mean for the plant-based meat industry?**
- **Will cell-based seafood really help ocean conservation? Some experts say cellular agriculture is not an easy solution to such a complex challenge.**

At the same time, oceans are becoming less habitable for aquatic life. They absorb anthropogenic CO_2 emissions and excess heat from the climate system. Ocean temperatures continue to break record highs, threatening ecosystems and killing coral reefs around the world. Every year, an estimated 5 to 12 million metric tons of plastic enters the ocean. The waste breaks down into microplastics which get eaten by fish and, eventually, us.

With all that troubles the ocean, and given the successful development of other cell-based meats, it is no surprise that companies are interested in commercializing seafood made in bioreactors. Lou Cooperhouse, president and CEO of BlueNalu, a cell-cultured seafood company in San Diego, California, USA, started his company to address these issues.

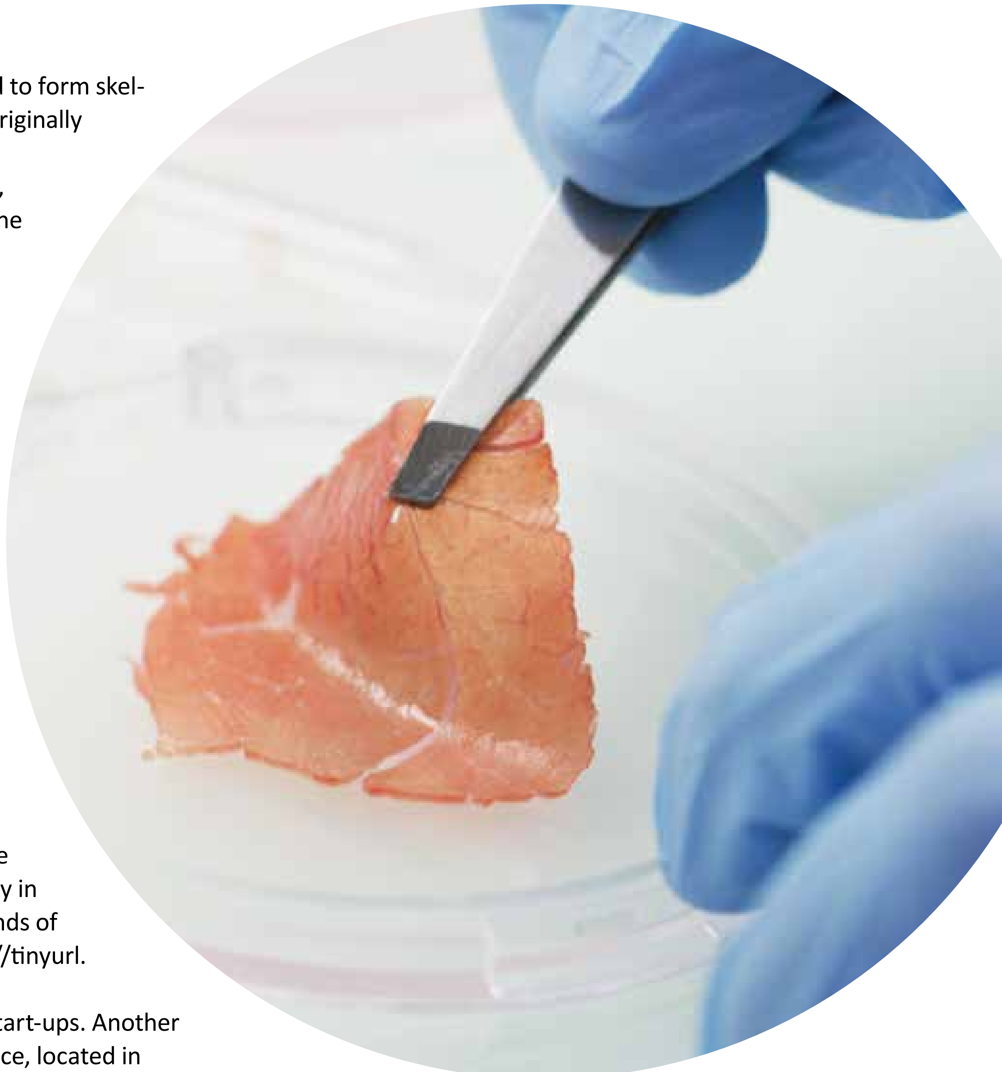
"I realized that cell-cultured seafood could represent an amazing solution and have the most transformative potential in the entire global protein category," Cooperhouse said.

When he started BlueNalu, he had worked in food innovation for 35 years and was inspired by the technical advances in manufacturing high-quality protein products through cellular agriculture.

Mimicking beef or chicken involves producing only one type of meat, but hundreds of thousands of different species populate the ocean. Will new food companies be able to cost-effectively produce cells differentiated into cod instead of tuna, or salmon instead of shrimp? Perhaps a more important question is whether cell-based seafood will really help with conservation efforts. Not everyone is so sure.

CELL-BASED SEAFOOD STATUS AND PROJECTIONS

Just like the technology used to culture beef and poultry, food start-ups make fish using stem cell biology and tissue engineering. A researcher extracts a biopsy-sized sample of muscle tissue from an animal and isolates pluripotent stem cells. These multifunctional stem cells proliferate in a bioreactor stew fortified with a proprietary mix of nutrients (sugars, salt, amino acids, vitamins). When the muscle cells have replicated



to a large enough population, they are grafted to form skeletal muscle-like structures using techniques originally designed for medical applications.

Cell-based meats have developed quickly, but the products still have a long way to go. The technology will need significant advances for companies to eventually mass-produce filets resembling wild-caught seafood. Researchers are working on edible scaffolding to grow tissue in the striated form of muscle. Until that development is commercialized, some companies are relying on 3D printing to give their products the structure consumers expect (https://tinyurl.com/2pvzew7r). For now, most cell-based meat companies have just opted to sell products like burgers, nuggets, and cakes that work best with their current capacity to produce cell clusters (Table 1).

Cooperhouse is undeterred. In an interview with National Public Radio (NPR) two years ago, he said he plans to scale up his cell-based technology until the company can serve the needs of seafood consumers. He said he imagines a 150,000-square-foot facility in every city that meets the consumption demands of more than 10 million nearby residents (https://tinyurl.com/3bb7wyse).

Scalability is advancing slowly for these start-ups. Another cultured seafood company, Cultured Decadence, located in Wisconsin, USA, plans to make lobster meat. After a year in production, they can make about half a gram from their reactors (https://tinyurl.com/25vyz3mt). They hope to increase output enough to provide public taste tests in the next 12 months. The cost of nourishing fish cells has been reported as the biggest factor limiting expansion.

"Fish derived omega-3s and other nutritional benefits from what they eat," says Cooperhouse. "As a result, the cell-cultured seafood we produce will have the same nutritional profile as conventional seafood."

Providing that nutritional profile comes at a cost. The concoction of salt, sugars, vitamins, and amino acids necessary for these cells to grow introduces a production expense that these start-ups must overcome to achieve their desired scaleup. In 2019, one cell-based company produced a single salmon

TABLE 1. A list of companies and their progress toward commercializing a cell-based fish product as of July 2020

Source: Halpern, B.S., *et al., Fish Fish.,00*,1–13,2021.

Company name	Location	Seafood type	Progress as of July 2020
Art Meat	Russia	Sturgeon	Developing their technology
Avant Meats	Hong Kong	Fish maw (dried swim bladder)	Anticipate taste tests of their fish maw in Q3 or Q4 of 2020
Blue Nalu	USA	Mahi-mahi, yellowtail	Held a tasting with multiple preparations in December 2019 of yellowtail product. Building a pilot-production facility
Cultured Decadence	USA	Crustaceans	Developing their technology
Finless Foods	USA	Bluefin tuna, carp	Held a tasting of carp croquettes in September 2018
Shiok Meats	Singapore	Shrimp, lobster, crab	Produced shrimp dumpling tasting for investors April 2019
Wild Type	USA	Salmon	Produced enough salmon for a group tasting in July 2019

sushi roll for USD$200 when the market value for wild-caught salmon at the time was between USD$5–9 per kilogram.

While companies try to find ways to reduce the expense of the growing medium for cell-based fish, they are also concerned with whether they will be allowed to call their product fish. Governing agencies worldwide are in the process of deciding how to regulate cellular agriculture.

CHALLENGES WITH REGULATIONS

Regulations on cultured products vary by country, but typically include monitoring of production, packaging, labeling, and marketing. In Europe, cell-based products fall under the European Union Novel Food Regulation. In the United States, based on a decision announced in 2019, these products will be regulated jointly by two agencies. The Food and Drug Administration (FDA) will regulate cell isolation, storage, growth, and maturation. Once cells and tissue have been harvested, the US Department of Agriculture (USDA) will oversee the remaining commercialization and labeling process.

Labeling is a controversial issue. Producers argue that they have the right to call their product meat, while the US Cattlemen's Association and other groups argue that labeling such products as meat misleads the public. The US Federal Meat Inspection Act refers to meat as "any product… made wholly or in part from any meat or portion of the carcass," which seems to justify the label. However, 12 US states have laws restricting the term "meat" on cell-based products (https://doi.org/10.1038/s43016-020-0112-z).

In late 2020, Singapore's Food Agency was the first to approve cell-based or cultured meat for a chicken product in that country that was poised to enter the market this year. The approval was expected to be a watershed for approvals from other countries, but that remains to be seen.

Updates to current regulatory procedures will likely be necessary to keep up with advancing technologies. For example, new scaffold materials for growing filets more efficiently may be developed in the future, requiring revised oversight. And companies may eventually want to genetically modify (GM) cells, which would lead to a reevaluation of how the products are regulated. A new FDA provision categorizes a product created through the manipulation of animal DNA as a drug (https://escholarship.org/uc/item/3k48n1gr). While the Food Safety Authority has approved GM food production, contingent on thorough safety assessments, many European countries (e.g., France, Germany, Greece) have banned the production and sale of GM foods. For now, no start-ups have proposed adopting such new technologies.

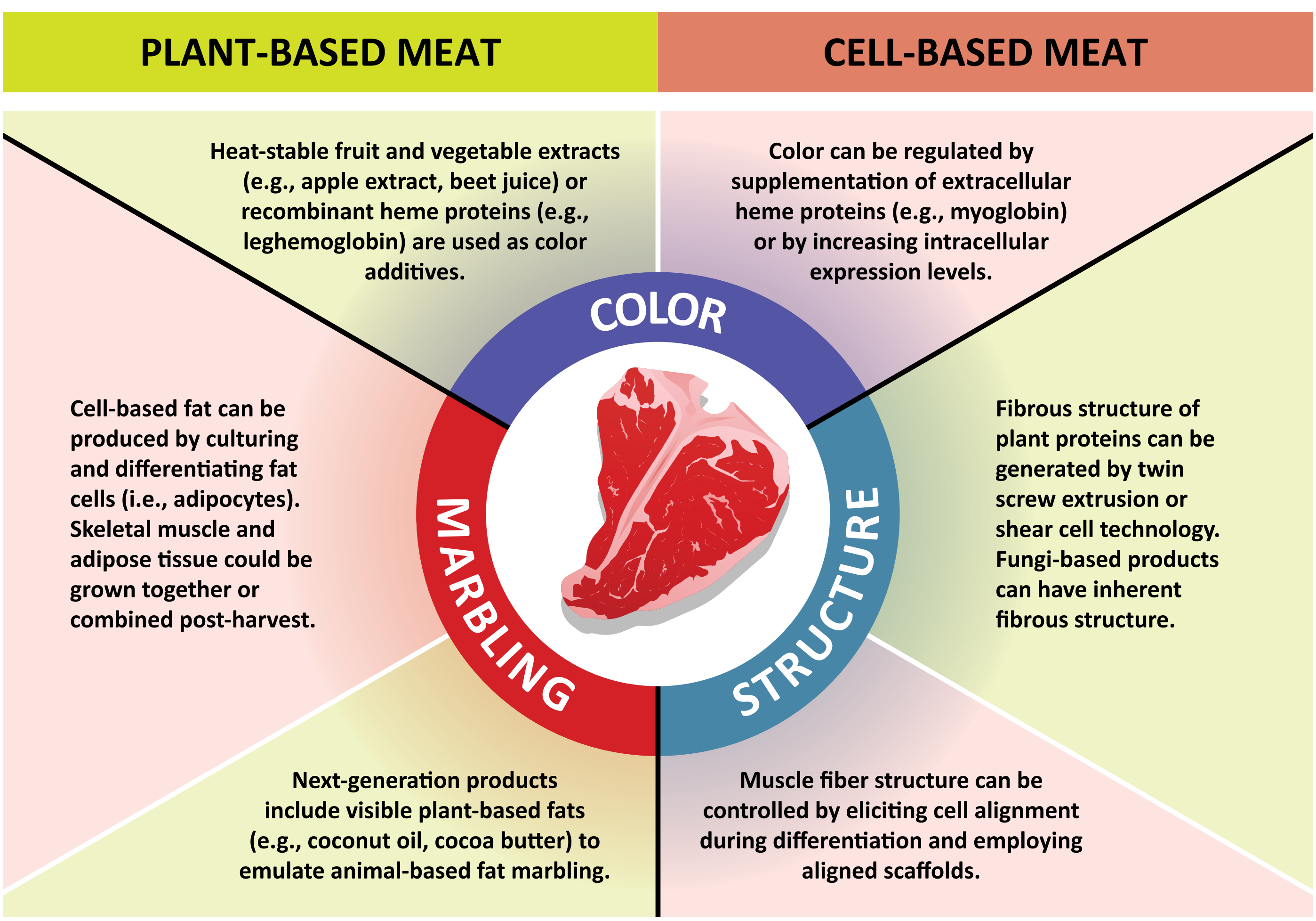


FIG. 1. Comparison of how plant- and cell-based products mimic the properties of animal meats. Source: Rubio, N.R, *et al.*, *Nat. Commun.*, *11*, 6276, 2020.

CELL- VERSUS PLANT-BASED

Cultured meat products will obviously compete with conventionally raised animals for consumer dollars, but they will also face-off against the existing plant-based market. Simple derivatives from soybean or wheat were developed in Asia thousands of years ago. Since then, plant-based meats have been designed to replicate the flavor, texture, and nutritional value of animal meat. In recent decades, scientists have developed several food processing technologies to improve plant protein functionalities and product formulations.

A company in Leipzig, Germany, called Bells Flavors & Fragrances has just launched a portfolio of flavor-masking compounds for plant-based dairy, meat, and fish products. A common complaint from plant-based consumers is the experience of off-notes that diverge from the conventional products these plant-based products aim to duplicate. Organoleptic compounds, (molecules that affect a product's sensory profile) are now being addressed by several companies like Bells Flavors & Fragrances (https://tinyurl.com/3kdm96jx).

Protein sources for plant-based products are relatively inexpensive; however, the post-harvest processing and formulation advancements needed to duplicate the consumer experience of eating meat can be rather pricey. Plant-based fats, flavor enhancers, and color additives drive up the cost of these meat alternatives. Still, they are presently far more affordable than cell-based meats. Although cell-based meats have the advantage of texture and taste being identical to the real thing, the plant-based market is far ahead in terms of establishing a consumer base (Fig.1).

An April report for the Good Food Institute (GFI) states that total plant-based retail sales reached \$7 billion and grew 27% over the past year—almost two times faster than total US retail food sales. This is a continuation of a growing market trend that has been observed for the past three years. More specifically, the report indicates that sales of plant-based meats crossed the billion dollar mark in 2020, reaching \$1.4 billion worth by year's end (https://tinyurl.com/4vzm92ws).

Food policy and food security experts like GFI see no reason to show a preference for one type of fish alternative over the other. They hope that consumer adoption of new cell-based products will not be price prohibitive much longer. Multiple sources result in a range of products serving unique segments of the consumer market.

Plant-based diets have evolved beyond traditional vegetarian and vegan fare as more people choose to avoid animal protein. This growth can be credited to flexitarian and younger consumer groups who are eager for a variety of environmentally responsible food options. However, some experts caution that cell-based seafood may not be the conservation miracle consumers seek.

CONSERVATION EFFORTS FUTILE?

Over the past half-century, the technical capacity, geographic coverage, and processing volume of fisheries have expanded enormously around the world. All fishing industry stakeholders agree that the overfishing crisis is the primary threat to ocean biodiversity (https://doi.org/10.1126/sciadv.abb6026). With millions of people consuming seafood as their protein source and the global population surging toward 10 billion by 2050, the world needs assurance that fish will be a reliable resource for our future.

Twenty years ago, Unilever and the World Wildlife Fund (WWF) set up an independent not-for-profit known as the marine stewardship council (MSC) to address concerns about overfishing. Today, there are more than 400 MSC certified fisheries worldwide. The certification is meant to assure buyers, retailers, and general consumers that their wild-capture fishery conforms to internationally recognized standards for environmental sustainability. The recent FAO report on the state of the world's fisheries indicated that in 2020, 78.7% of wild-caught seafood came from sustainably managed fisheries.

In consumer surveys, people say they take a product's sustainability into account when making a purchase (https://tinyurl.com/k8kusw9s). This behavior has increased by 10% during the pandemic, with consumers saying they are now more conscious of the environment. One of the sustainable shifts many consumers are making is in their dietary choices, eating vegan, for example, to circumvent practices they perceive to be cruel to animals or unsustainable. Researchers at the University of Santa Barbara, California, question whether such choices can really have an impact on a conservation problem like overfishing.

In a recent journal article, the team argues that the best path to achieving ocean conservation is not through the development of a cell-based seafood alternative (https://doi.org/10.1111/faf.12541). To achieve such a goal, the product must first make it onto the market, a feat in and of itself. Cell-based seafood would then need to become so desirable that demand for wild-caught seafood decreases and fish stocks rebound.

The paper's authors argue that for this outcome to prevail, fishers would need to find other careers, and the cultural acceptance of bioreactor-produced fish would have to dramatically increase—assuming that this technology can be developed on a large scale at a lower price than wild-caught fish which, as previously mentioned, is currently not the case.

Until the costs come down, cell-based seafood will have a difficult time breaking into the market. And even then, research results indicate plant-based products could be more popular. Surveys gathered from consumers who received information on the sustainability of conventional, plant-based, and cell-based meat led researchers to predict respective market shares of 72%, 23%, and 5% for each (https://doi.org/10.1016/j.foodpol.2020.101931). A market forecast by the US management consulting firm Kearney had a more positive outlook for cell-based meat and predicted that in the next 20 years the market share would be split about evenly between the three (https://tinyurl.com/avxzszr2).

If conservation does not win consumers over, cell-based seafood can certainly claim to be clean. Cells grown in a bioreactor are not exposed to the mercury or microplastics pollution from the ocean. Consequently, the fish products they form will be guaranteed toxin-free. That could be enough of an incentive for fish eaters to convert from conventional products.

Cooperhouse says he is not looking to replace wild-caught or farm-raised seafood but is aiming to become a third alternative for vegan and vegetarian seafood eaters (https://tinyurl.com/3bb7wyse). "Consumers are changing. They are looking at health. They are focused on the planet," Cooperhouse said to NPR. "This is not a fad or a trend — this is happening."

Companies focused on plant-based products as meat alternatives will want to keep an eye on the growth of the cultured meat industry. If forecasts are correct, they can expect competition from this sector in the coming decade.

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Epoxidation in moderation brings new life to old pavements

Eric W. Cochran

- Viscous and polar, epoxidized soybean oil has been passed over as an asphalt additive, particularly as a “rejuvenator”.
- Asphalt rejuvenators are recycling aids that restore virgin-like properties to aged and brittle binders. Oxidation causes physical and chemical fusing of asphalt molecules over time, especially aromatics and asphaltenes.
- Tuning the oxirane content in partially epoxidized soybean oil balances viscosity, asphalt compatibility, and reactivity with aged molecules. This enables the formulations of reactive restorative modifiers (RRMs)—rejuvenators that pave the way for highly recycled asphalt without compromise.

Asphalt pavements are nearly everywhere: In the United States, about 7 million acres of roads, parking lots, and playgrounds feature an asphalt surface. Pavements are extremely energy-intensive materials, with each acre paved (about 1 lane-mile) requiring 1.3 trillion Joules (TJ), the energy stored in 1,500 barrels of oil. If all 400,000,000 tons of domestically installed asphalt in 2019 were sourced from virgin materials, the associated energy consumption would exceed 5 quadrillion BTUs, or more than 5% of the total annual energy consumption in the United States.

While asphalt pavements are only slightly less energy intensive than Portland cement concrete, they offer a far greater potential for recycling. RAP (reclaimed asphalt pavement) is produced during the demolition phase of a “mill-and-fill” construction operation. Feeding the RAP back into the new hot mix brings the obvious benefits of reduced raw material costs and environmental impacts. With the proliferation of light crudes that produce no asphalt and the ever-increasing efficiency with which refiners process heavy crudes, the supply of paving-grade asphalt struggles to keep up with demand, further reinforcing the need to maximize recycling.

The degree to which RAP can be reused in new construction is limited by its impact on hot mix workability, its ability to mix well with virgin material, and the susceptibility to cracking it introduces to the newly constructed pavement. RAP's brittleness is mainly driven by the molecular changes imparted through years of exposure to heat and oxygen.

Asphalt is the viscous residue left behind after the processing of heavy crude oil. It is composed of thousands of unique molecules—mainly hydrocarbons with sulfur, oxygen, and nitrogen—ranging from hundreds to a few thousand grams per mole in size. The heaviest molecules are polyaromatics known as asphaltenes; in virgin asphalt these are suspended as solid colloidal particles tens of nanometers in diameter. The lighter molecules, known as "maltenes", range from oily hydrocarbons to sticky polar aromatic resinous compounds. In a paving-grade asphalt, the asphaltene-maltene composition is balanced to provide a workable fluid at production temperature, ≈ 150°C, load-supporting structure up to 50–80°C (depending on climate), and stress-dissipating ductility in cold weather < -10°(C).

As asphalt ages, its balanced composition shifts. Over time, asphaltenes enrich their aggregation state in an inexorable march toward equilibrium. Oxygen inserts itself throughout the composition, particularly in susceptible aromatic species and branched hydrocarbons, yielding ketones, aldehydes, acids, and sulfoxides. These polar species further exacerbate aggregation and heterogeneity, making the aged asphalt stiff, brittle, and less miscible with virgin asphalt and important additives like polymers.

ENTER REJUVENATORS

If aging is to stiffen and embrittle, then a "rejuvenator" is an additive designed to soften and toughen. While a simple concept, the asphalt industry has struggled to properly quantify the characteristics of a rejuvenated pavement. Pavements fail largely through two mechanisms: rutting and cracking. The former occurs through plastic deformation under load while the binder is too soft, whereas the latter manifests over time and is accelerated in cold conditions.

The Superpave criteria emerged in the 1990s, formalized by the American Association of State Highway and Transportation Officials (AASHTO) M 320 specification. Essentially, the binder dynamic shear modulus and flexural creep stiffness determine upper and lower temperature "Performance Grades" (PG) intended to be predictive of the rut and crack resistance of the pavement. According to this measure, any additive that softened the pavement dropped its low PG grade (PG-L), ostensibly improving its crack resistance.

Re-refined Engine Oil Bottoms (REOB), first introduced in the 1980s to counteract the stiffness of asphalt residues produced under aggressive vacuum distillation (vacuum tower bottoms), was widely used in this manner to enable RAP use while keeping PG-L low. Over the years, however, owner-agencies noted serious cracking problems with many of their higher-RAP pavements, especially in the northern climes of Ontario and New England. Many of these low-performing contracts were later found to be correlated with the presence of REOB, which in many jurisdictions has led to a widespread ban on rejuvenating additives.

Concurrently, the asphalt research community has directed intensive efforts to developing testing protocols that are more predictive of cracking than the PG-L metric. A relatively simple methodology states have begun to adopt is a new parameter, ΔT_c (delta tee see), derived from the same creep stiffness test specified by M 320. In this test, a coupon of asphalt binder is deformed in a 3-point bend geometry at reduced temperature by a "bending beam rheometer". The rheometer measures the creep stiffness as a function of time after the application of a step stress; at 60 s, the stiffness and rate of stiffness reduction are the reported parameters. M 320 specifies that the asphalt binder passes the test if $S \leq 300$ MPa and $m \geq 0.3$ MPa s^{-1}. Two temperatures T_s and T_m thus define the temperatures below which an asphalt fails based on stiffness or relaxation rate, respectively. While PG-L is the maximum of these, $\Delta T_c \equiv T_m - T_s$ recognizes the superior alignment of the creep relaxation rate with ductility. A significant and growing body of work has shown that in pavements where $\Delta T_c < -5$°C, premature cracking is statistically far more likely.

Another emerging family of specifications known as "Balanced Mix Design", as defined by a 2015 Federal Highway Administration task force, adapts fracture mechanics tests to fully formulated pavements. Figure 1 (page 14) illustrates three of the most common configurations: the disk-shaped compact tension (DCT) test, the Illinois flexibility index test (I-FIT), and the indirect tension asphalt cracking test (IDEAL-CT). While these tests differ in the deformation mode, testing environment, and data reduction practices, they all directly assess the cracking tendency of pavement through the fracture energy.

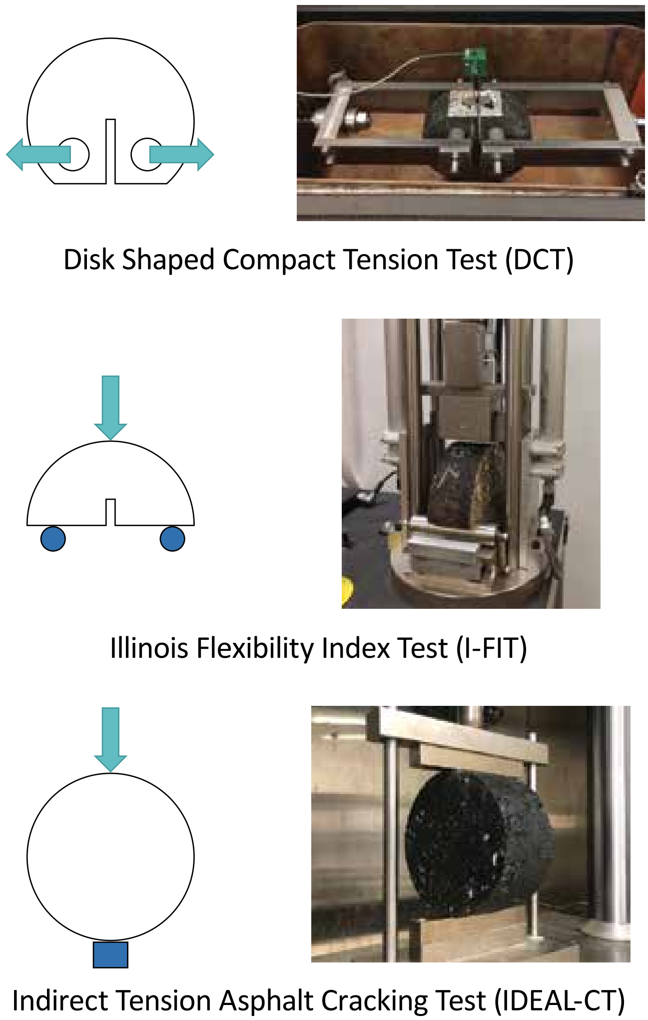

FIG. 1. Fracture energy measurement techniques in the asphalt paving industry

RESTORING ASPHALTENE BALANCE, PERMANENTLY

These advances in testing methodology represent significant progress in the early detection of crack-prone pavement designs, potentially eliminating rejuvenation strategies that only superficially address RAP-embrittlement through a reduction in the binder melt viscosity. This is particularly important as a variety of new rejuvenators have come to market. Many options are now available, ranging from light aromatic and paraffinic oils to tall oil derivatives, distiller's corn oil, soybean oil, and vegetable oil oligomers. Through plasticization, these products successfully reduce the PG-L value of RAP modified pavements, while at the same time more aggressively dropping the PG-H value, which sets a dose rate beyond which rutting susceptibility becomes a concern.

Ideally, the objective of rejuvenation is to rebalance the asphaltene-maltene content of binder. In the short term, plasticizing rejuvenators with good asphaltene solvency will be effective in breaking up and distributing asphaltene aggregates. Vegetable oils like soybean or corn oil are particularly effective in this regard. However, without intervention, the dispersed asphaltenes are free to re-agglomerate through diffusion in the days and months after construction.

Our innovation in this regard is to arrest this process through surface passivation as illustrated in Figure 2: When an aged asphaltene agglomerate encounters rejuvenator molecules (2a), solvency alone will disperse them, reducing their volume as measured by small angle X-ray scattering by at least 30% (2b,2c). The acid and sulfoxide groups on the asphaltene surfaces can be used as functional handles to *permanently* graft rejuvenator molecules. The interparticle attractive interactions are diminished, and the compatibility of the modified asphaltenes with the maltene matrix is improved (2d). We term rejuvenators that act in this manner "reactive restorative modifiers" (RRMs).

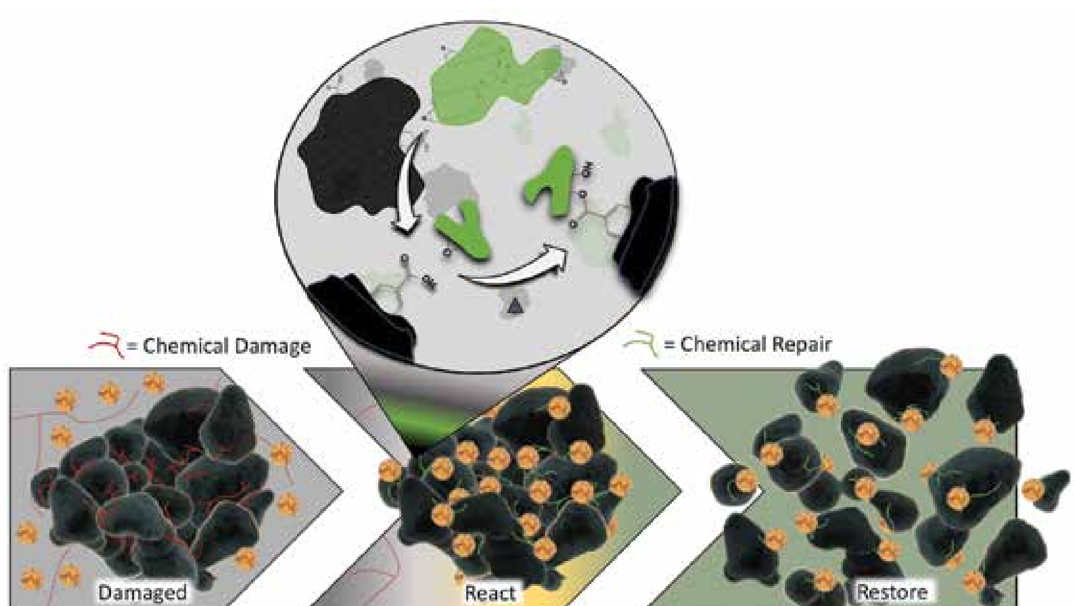

FIG. 2. Sub-epoxidized soybean oil (SESO) as a reactive restorative modifier (RRM) for asphalt. (a) Aged asphalt is rich in agglomerated and oxidized asphaltenes. (b) RRM rejuvenators like SESO solvate these agglomerates and then (c) chemically bind to them to prevent re-aggregation. (d) The resultant pavement has a stable and balanced asphaltene dispersion.

As far as the chemistry is concerned, epoxidized soybean oil (ESO) is a natural RRM due to the high reactivity between oxiranes and acids. Unfortunately, the viscosity of commercially produced ESO is too high to provide sufficient plasticization as an asphalt rejuvenator. Moreover, its high polarity provides limited solubility with asphalt and poor RAP solvency.

Soybean oil, on the other hand, has excellent solvency and plasticization potential, although it lacks the requisite reactivity. A straightforward solution, then, is to modify the degree of ESO epoxidation to provide a balance of plasticization, solvency, and aged-asphaltene-passivating oxirane chemistry. To this end, sub-epoxidized soybean oil (SESO) was developed at Iowa State University as an RRM and first evaluated in the lab. Binder testing with up to 50% RAP-extracted binder showed $\Delta T_c \geq {}^{-}5$°C was easily achieved by formulating the SESO dose rate. By leveraging existing commercial vegetable oil epoxidation assets, we were able to take SESO to the field, completing demonstration projects on county roads and parking lots in nine states throughout the United States. Hundreds of binder extracts and as-produced mix samples were evaluated for crack performance according to ΔT_c, DCT, I-FIT, and IDEAL-CT metrics.

Statistical analysis yielded a comprehensive model, sampled in Figure 3, to predict pavement performance as a function of RAP content and base binder type. In our field work, we were able to push RAP utilization as high as 45%, limited only by the standard production hardware in use at hot mix plants. In the future, modifications to the hot mix process could enable the routine placement of pavements with 50% RAP or higher.

This work caught the attention of Colorbiotics, a leader in construction specialty chemicals, which is building its portfolio of products to promote sustainable construction practices. Invigorate™, an asphalt rejuvenator (Fig. 4), was formulated using SESO and is looking to revolutionize the use of RAP in the asphalt paving industry.

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FIG. 4. Colorbiotics is using RRM technology in Invigorate™, an asphalt rejuvenator featuring SESO in its formulation.

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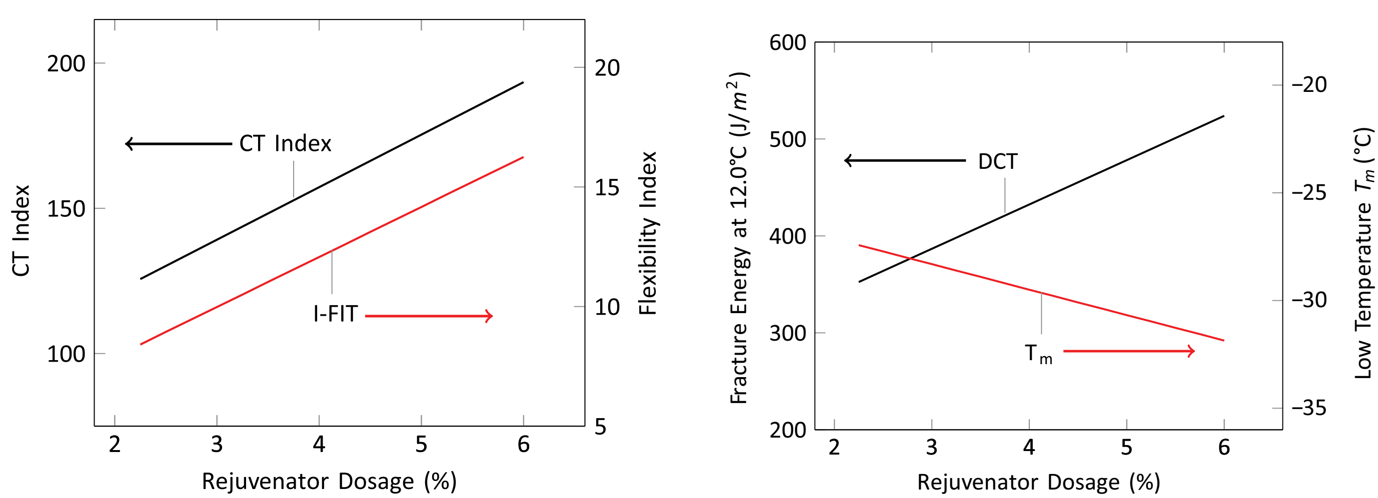

FIG. 3. SESO performance as a function of dose rate (wt % with respect to total asphalt cement) in a 40 % RAP mix design using a PG64-22 base binder

influencers, directing the field and product.

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Stabilization of omega-3, PUFA-rich raw materials and foods against lipid oxidation

Charlotte Jacobsen

- **It is still a challenge to protect complex food emulsions, such as mayonnaise, against lipid oxidation—particularly when they are enriched with fish oil. This is at least partly because it is hard to predict antioxidant efficacy in these systems from studies in simple emulsions.**
- **Strong metal chelators are required to protect mayonnaise and dressings with egg yolk as emulsifier against lipid oxidation.**
- **Peptides with metal-chelating properties may be new antioxidant candidates for this purpose, but a better understanding of the relationship between their chemical structure and efficacy is needed.**

Charlotte Jacobsen is the winner of the 2021 Stephen S. Chang Award which recognizes a scientist, technologist, or engineer who has made distinguished accomplishments in research for the improvement or development of products related to lipids. Her open-access award presentation was given in March 2021 as part of the of the AOCS Awards Presentation Award Series.

My lipid oxidation journey started in the mid-1990s, when my research group attempted to enrich mayonnaise with fish oil due to the beneficial health effects of the long-chain omega-3 fatty acids. Our first studies clearly showed the necessity of protecting fish-oil-enriched mayonnaise against oxidation, because nasty, rancid, and fishy off-flavors developed quickly, even when the mayonnaise was stored at 5°C. Therefore, evaluation of a wide range of antioxidants was initiated (Table 1). For some of the antioxidants, we also studied their partitioning into the oil and water phases as well as the interface.

At about the same time, William Porter and later also Edwin Frankel proposed the Polar Paradox theory, which stated that polar antioxidants are more effective in less polar media such as bulk oils, while non-polar antioxidants are more effective in relatively more polar media, such as oil-in-water emulsions. From this hypothesis, one might expect to find a difference in the efficacy between ascorbic acid and ascorbyl palmitate as well as between gallic acid and propyl gallate, and maybe even between oil-soluble and water-soluble tocopherol preparations when applied in mayonnaise. However, none of these antioxidants efficiently prevented lipid oxidation in fish-oil-enriched mayonnaise. The water-soluble metal chelator EDTA was the only antioxidant which very efficiently inhibited lipid oxidation. We discovered that lipid oxidation in mayonnaise is catalyzed by iron from egg yolk located at the oil-water interface, which is released or activated due to the low pH in

TABLE 1. Overview of the efficacy and partitioning of some commercial antioxidants in fish-oil-enriched mayonnaise evaluated by Jacobsen's research group. In the column "Polarity": Blue color indicates results from partitioning studies. Orange and black colors indicate the expected location of the antioxidant, but it was not determined.

Antioxidant system	Polarity (partitions into)	Antioxidant principle	Activity
Ascorbic acid	Water	Scavenge free radicals and oxygen	Prooxidant
Ascorbyl palmitate	Interface?	Scavenge free radicals and oxygen	Prooxidant
Gallic acid	Water >> interface	Free radical scavenger	Prooxidant
Propyl gallate	Oil > interface > water	Free radical scavenger	Prooxidant
Oil-soluble tocopherol preparation	Oil >> interface	Free radical scavenger	Weak antioxidant/ Prooxidant
Water-soluble tocopherol preparation	Oil >> interface	Free radical scavenger	Weak antioxidant/ Prooxidant
Lactoferrin	Water & interface?	Metal chelator	No effect or prooxidant
EDTA	**Water**	**Metal chelator**	**Strong antioxidant**

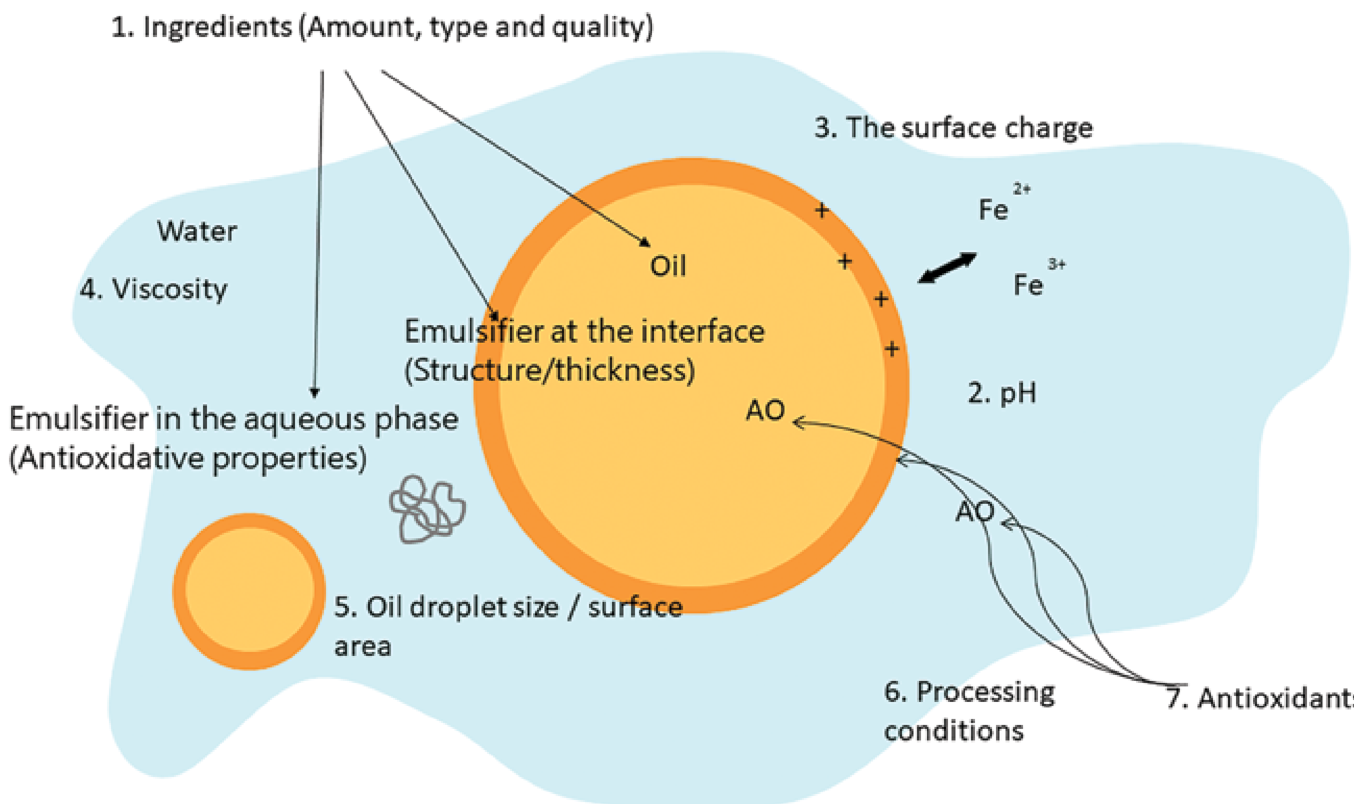

FIG. 1. Important factors affecting lipid oxidation in emulsions. From Anna F Horn's PhD thesis, Technical University of Denmark.

mayonnaise. Therefore, a strong metal chelator such as EDTA is required to inactivate iron present in the aqueous phase. Free radical or oxygen scavengers cannot do the job alone irrespective of whether they are located in the water, oil, or at the interface.

Later, we studied lipid oxidation mechanisms in fish-oil-enriched milk. One of our studies concerned the effect of the homogenization conditions and composition of the oil-water interface on lipid oxidation. It is well known that lipid oxidation increases with increasing temperature. Some studies have also found that lipid oxidation increases with increasing interfacial area in emulsions, because a larger interfacial area will increase possible interactions between transition metal ions (such as iron) in the aqueous phase and already existing lipid hydroperoxides located near the oil-water interface inside the oil droplet, whereby lipid oxidation is promoted.

Therefore, we expected that if we increased homogenization temperature and pressure—whereby the interfacial area increased due to the formation of smaller droplets—then lipid oxidation would also increase. However, the opposite was the case, as the best oxidative stability was obtained when a high temperature and pressure was used. Further studies on the protein composition of the oil-water interface revealed that it was significantly affected by the homogenization conditions. Thus, when high temperature and pressure were applied, more beta-lactoglobulin was located at the interface and more casein was found in the aqueous phase. Hence, the results suggested that such a distribution of these two proteins was favorable in terms of preventing lipid oxidation, and that this was more important than the temperature during homogenization and the droplet size obtained.

Based on our own studies and others, such as those by Eric Decker's lab at the University of Massachusetts, Amherst, USA, we proposed the model shown in Figure 1 to explain some important factors that can affect lipid oxidation in emulsions. The figure illustrates that the interface is indeed important for lipid oxidation, but also that the presence of excess emulsifiers in the aqueous phase and interaction between pro-oxidants and antioxidants and ingredients located in the different phases can play a major role.

To further study the role of the location of the antioxidants in food emulsions, we have collaborated with Pierre Villeneuve's lab at CIRAD in France on the use of phenolipids, polar antioxidants that have been lipophilized by conjugation with alkyl chains of different lengths. Villeneuve and his group proposed the "cut-off theory," which in brief says that the efficacy of a polar antioxidant in emulsions will improve with increasing length of the alkyl chain until a certain point after which the efficacy will decrease again. When the phenolipid has the optimal chain length, most of the antioxidant molecules will be located at the oil-water interface.

Villeneuve's group also developed the CAT assay, which is based on a micro-emulsion system with tung oil from *Vernicia fordii* (stripped; no tocopherol), and Brij 35 as emulsifier and 2,2′-azobis-2-methyl-propanimidamide, dihydrochloride (AAPH) as oxidation initiator to evaluate the antioxidant efficacy of a wide range of phenolipids. We used the same CAT assay to determine the optimal chain length of caffeate esters and found it to be 8–12. We then determined the optimal chain length of the caffeate esters in fish-oil-enriched milk and mayonnaise. For milk, the optimal chain length was very different from that of mayonnaise and the CAT assay. Thus, a chain length of 1 and 4 turned out to be most efficient. A similar result was obtained with ferulic acid esters where a chain length of 1 and 2 was the most efficient. In mayonnaise, the optimal chain length was between 4 and 12. We therefore concluded that the optimal chain length is affected by interactions between the phenolipids and other ingredients in the food system, and therefore the optimal chain length cannot be predicted from the CAT assay.

Most studies on phenolipids have been conducted with stripped oil containing no tocopherol. Because tocopherols are (always) present in real food emulsions, we investigated the effect of the presence of endogenous tocopherol on the "cut-off" effect in oil-in-water emulsions prepared with Tween as emulsifier and with caffeates as antioxidants. Interestingly, we found that the presence of tocopherol had a large effect. When tocopherol was present, the optimal chain length was C0 (i.e., caffeic acid), whereas C0 was a prooxidant in the absence of tocopherol, where caffeates with a chain length of 1 to 20 were the most efficient antioxidants. We also investigated the partitioning of the different caffeates in the presence and absence of tocopherol. Based on the results we proposed that when tocopherol is present, caffeic acid is a good antioxidant because it can regenerate tocopherol at the interface, whereas caffeates to some extent will be localized in micelles in the aqueous phase.

Antioxidants can also be conjugated to emulsifier molecules, thereby increasing their presence at the interface compared to when they are in their unconjugated free form. This principle is illustrated in Figure 2 for caffeic acid conjugated to DATEM with different chain lengths (C12 and C14). In collaboration with Zheng Guo's group from Aarhus University, Denmark, we compared the oxidative stability of 70% fish-oil-in-water emulsions prepared with a mixture of caseinate and DATEM (total concentration 2.8 %, ratio: 2:1) as emulsifiers. We replaced 10, 30, or 60% of the DATEM with conjugated DATEM-caffeic acid and compared the antioxidative effect of the conjugated caffeic acid with corresponding concentrations of unconjugated caffeic acid. Results showed that the highest oxidative stability was obtained when 60% of the DATEM was replaced with conjugated DATEM-caffeic acid, suggesting that caffeic acid was more efficient when it was located at the interface in its conjugated form compared to when it was present in its free form. A chain length of C14 provided the best protection. We subsequently found that addition of a delivery emulsion with the DATEM-caffeic acid conjugate (C14) to fish-oil-enriched mayonnaise also offered some protection against lipid oxidation, but it could not prevent the formation of fishy and rancid off-flavors.

Several studies have reported on the antioxidative and emulsifying properties of peptides from different raw materials using a trial-and-error approach, without *a priori* knowledge about the amino acid sequence of the peptides, which could provide such activity. We have used another approach. Thus, we employed quantitative proteomics for identification of abundant proteins followed by bioinformatic prediction using tools such as EmulsiPred (available at https://github.com/MarcatiliLab/EmulsiPred to identify a number of highly functional emulsifier peptides and AnOxPePred (available at https://services.healthtech.dtu.dk/service.php?AnOxPePred-1.0) to identify peptides with antioxidant properties from single cell proteins, rubisco and protein-rich side-streams from potato and red seaweed. Subsequently, we validated the emulsifying and antioxidant properties in different assays using synthetic peptides with the same sequence as those embedded in the proteins from the four raw materials. Finally, we evaluated the emulsifying and/or antioxidant properties in

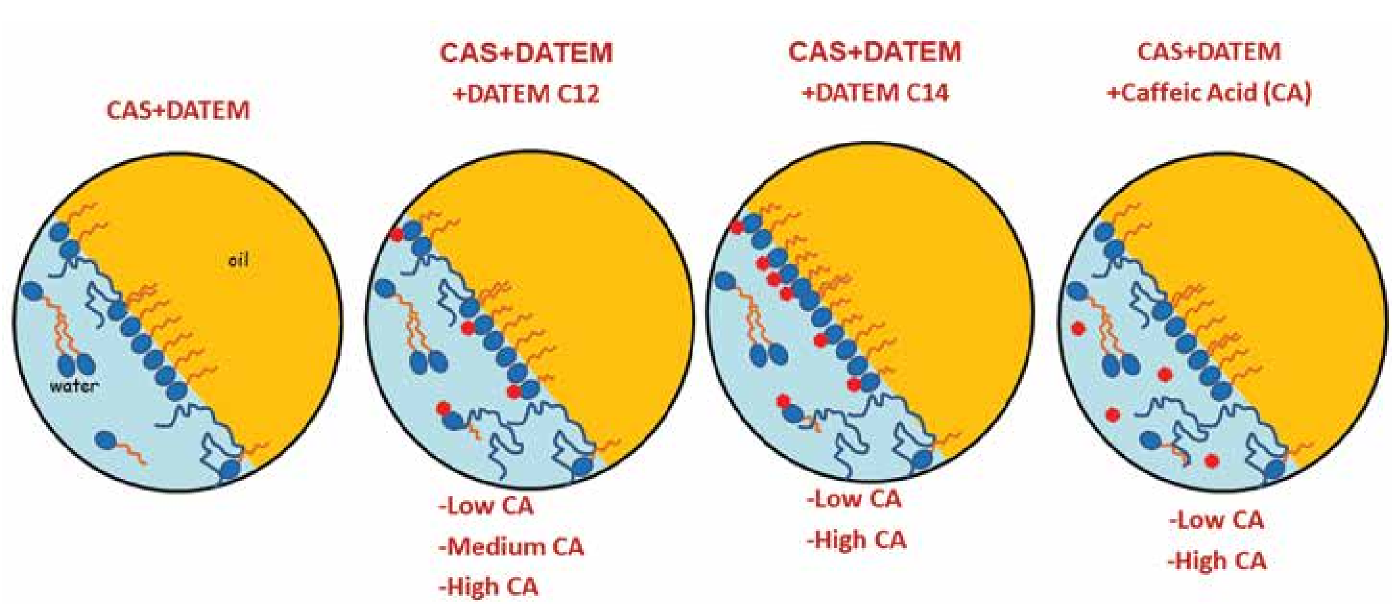

FIG. 2. Expected location of DATEM (blue molecules), free caffeic acid (red molecules), and conjugated DATEM-caffeic acid (blue molecule with red molecule attached) in 70% oil-in-water emulsions. Courtesy of Betül Yesiltas, Technical University of Denmark.

5% oil-in-water emulsions prepared in larger scale using microfluidizer homogenization. Selected antioxidant peptides were also evaluated in mayonnaise. We were able to confirm that peptides, which had been identified to be the most promising in the small-scale emulsifier assays also performed well in larger-scale assays. Interestingly, we found two peptides, which both provided good physical and oxidative stability. Likewise, we found several peptides predicted to be antioxidants, which were confirmed to have good antioxidant effects in emulsions at pH4 and 7. Some of them also reduced lipid oxidation in fish-oil-enriched mayonnaise, but none of them were as good as EDTA. Nevertheless, these studies show that our new approach can be used to identify antioxidant peptides from protein-rich side streams, which is interesting from a circular bioeconomy perspective.

Brown seaweed is a rich source of polyphenolic compounds with antioxidative properties. We have extracted polyphenols from bladderwrack using different solvents and evaluated the antioxidative effect of the extracts in mayonnaise. In particular, water extracts from bladderwrack showed strong antioxidative effects in fish-oil-enriched mayonnaise, and we ascribed this to their good metal chelating properties. However, the extracts gave the mayonnaise a brownish color, and this issue needs to be resolved before the extract can be applied to protect mayonnaise.

I already mentioned that side streams from food production have a potential for use in the production of new food ingredients with functional properties. This is also the case for side streams from the seafood industry. Such side streams are, however, very susceptible to lipid oxidation due to the high proportion of polyunsaturated fatty acids in their lipid fraction. Therefore, they must be protected against lipid oxidation before they are transformed into new food ingredients for human consumption. We have collaborated with Ingrid Undeland, Chalmers Technical University, Sweden, on this issue. We found that rosemary-based extracts offer high protection against lipid oxidation in guts, heads, and frames from cod.

In conclusion, mayonnaise remains a challenge to protect against oxidation. EDTA is still the best commercially available antioxidant to protect mayonnaise against oxidation due to its strong metal chelation properties. However, extracts from seaweed with metal-chelating properties are promising new candidates as are peptides obtained from various food production side streams. Bioinformatics is a promising new tool for predicting antioxidant properties of peptides from such side streams, but more data are needed to further refine and optimize its prediction accuracy. Lipophilization of antioxidants or conjugation of emulsifiers with antioxidants are promising techniques to improve the efficacy of polar antioxidants in emulsions, but the optimal structure/chain length in food emulsions can currently not be predicted from model emulsions.

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Charlotte Jacobsen is professor in Bioactives–Analysis and Application. She leads the Research group for Bioactives–Analysis and Applications at the National Food Institute, Technical University of Denmark. Jacobsen is internationally renowned for her research in lipid oxidation of omega-3 rich foods and has received several awards in addition to the 2021 Stephen S. Chang Award, including the 2003 Danish Danisco prize ($40,000), the 2010 French La Médaille Chevreul awarded by Association Francaise pour l'étude des Corps Gras, the 2020 German DGF Normann Medaille, and two AOCS best paper awards. She was appointed by the European Food Safety Authority (EFSA) as an expert in the Fish Oil working group under the Biohazard Panel to evaluate the potential hazard associated with human intake of refined fish oil. She has led several large national and international projects, including the ongoing EU BBI JU project WaSeaBi. Her publication list includes more than 220 peer-reviewed manuscripts and book chapters.

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Hydraulic fluids, steam turbine oils, and transformer oils move toward biodegradability

Raj Shah, Amanda Loo, and Nathan Aragon

A shift toward "green energy" is becoming more popular as the knowledge of how mineral oil and hydraulic fluids affect the environment increases. Companies have begun studying alternative resources that can be used in place of these toxic fluids. Biodegradable fluids and renewable lubricants use eco-friendly resources, such as vegetable and crop seeds, esters, and glycols, to minimize damage to the environment and ecosystems. Steam turbine oils, hydraulic fluids, and transformer oils are major areas of focus for lubricating fluids due to their global usage. Attention to these kinds of fluids has resulted in numerous experiments and substantial progress toward converting to biobased lubricating fluids in these applications.

- **A shift toward "green energy" is becoming more popular as knowledge of how mineral oil and hydraulic fluids affect the environment increases.**
- **Steam turbine oils, hydraulic fluids, and transformer oils are major areas of focus for lubricating fluids due to their global usage.**
- **Biodegradable fluids demonstrate improved viscometry, better compressibility characteristics, and lower toxicity compared to mineral oil.**

EVOLUTION OF BIODEGRADABLE FLUIDS

In the United States, The Guidelines for Designating Biobased Products for Federal Procurement are defined by section 9002 of the 2002 Farm Bill. This section has been defined by the Food, Conservation, and Energy Act of 2008 as well as the Agricultural Act of 2014, or the 2008 Farm Bill and 2014 Farm Bill, respectively [1]. The guidelines are stated in 7 CFR part 3201. To be considered a biobased product, the product must have "renewable domestic agricultural materials and forestry materials" or feedstock/intermediate ingredient.

The BioPreferred Program established by the 2002 Farm Bill consists of 42 product categories with products meeting this requirement that are available for federal purchasing. The EU Ecolabel lists lubricants specifically, as a product group consisting of greases, hydraulic and chainsaw oils, two-stroke engine oils, and other lubricants [2].

Several tests are currently approved to determine biodegradability. The OECD 301B developed by the Organization for Economic Cooperation and Development (OECD), the CEC L-33-A-934 developed by the Coordinating European Council (CEC), and the ASTM D-5864 developed by the American Society for Testing and Materials (ASTM) are three of the major tests. The OECD and ASTM look at ready biodegradability, where 60% of the material is converted to CO_2 within 10 days, and the CEC looks at the biodegradability of hydrocarbon compounds [3].

Petroleum oils spilling into bodies of water is a particular concern that helped prompt a shift toward more biodegradable and safe alternatives to mineral-based fluids. The 1979 IXTOX I well released

140 million gallons of oil into the Gulf of Mexico's Bay of Campeche by the time the well explosion was under control in 1980. Later, the 2010 oil spill released approximately 210 million gallons of oil into the Gulf of Mexico [4]. The release of such massive amounts of harmful and toxic oil into bodies of water sparked a movement to use oils that are more eco-friendly.

The four different classifications of biofluids are hydraulic oil environmental triglyceride (HETG), hydraulic oil environmental ester synthetic (HEES), hydraulic oil environmental polyalphaolefins and related products (HEPR), and hydraulic oil environmental polyglycol (HEPG) [1]. Each classification grouping has distinct characteristics, such as temperature stability and biodegradability. Table 1 demonstrates direct comparisons of a rapeseed-based HETG and two kinds of HEES, saturated and unsaturated. In several categories, the biodegradable fluids demonstrate more optimum values in the different types of data available, such as viscosity and viscosity index. These advantages that the biodegradable fluids have over mineral oil have prompted their use in specific applications.

Bio-based biodegradable fluids are composed of carbon, hydrogen, and oxygen, and are typically triglycerides. The demand and market value of biodegradable and synthetic fluids has continuously grown over the decades, from a 3.5% market value in 1990 to an 8.0–10% value in 2002 [6]. The use of biodegradable fluids has demonstrated a significant shift of use in lubricants and other applications due to consistent environmental concerns.

TABLE 1. Characteristic comparisons of standard mineral oil and three biodegradable fluids [5]

Typical available data	Standard mineral oil	HETG (rapeseed-type oil)	Unsaturated HEES	Saturated HEES
Density @ 15°C (g/ml)	0.880	0.922	0.929	0.918
Flash point (°C)	204	255	198	240
Pour point (°C)	-29	-33	-36	-58
Viscosity @ 40°C (mm²/s)	32.0	34.0	35.0	31.8
Viscosity @ 100°C (mm²/s)	5.4	8.0	8.1	5.8
TAN (mg KOH/g)	0.96	0.40	0.60	0.70
Viscosity index	103–140	210–250	175–215	140–150
Iodine value	–	80–120	40–80	<10
Optimum temp range (°C)	<80	<60	<80	>80

USE OF BIODEGRADABLE FLUIDS

Biodegradable fluids and products have become more popular in recent years thanks to numerous studies that have been done to determine the effects of mineral oil and other non-biodegradable fluids on the environment. Figure 1 demonstrates how, through photosynthesis, biomass can be used to create biodegradable oils that can then be used in products and manufacturing applications. Eventually, these oils will disintegrate and go back into the environment in a safe manner, allowing the process to repeat.

There are currently five biodegradable base stocks available on the market for producers to use: polyalphaolefins (PAOs), high-oleic vegetable oils, dibasic acid esters, polyol esters, and polyalkylene glycols [8].

Vegetable oils can be used in a variety of functions. They have low toxicity, high viscosity index, and high shear stability [9]. Canola oil might be used in transmission fluids and food-grade lubes; high-oleic soybean oil and rapeseed are used in many greases and hydraulic fluids [10]. Jojoba, karanja, jatropha, and castor oil are beginning to be used for lubricant production because of a major concern that edible oils derived from seeds or plants of natural food chains will disrupt ecosystems. Using these alternate types of non-edible oils, as well as microalgae, can minimize the potential damage on existing ecosystems and food chains.

For renewable lubricants, high thermal stability, low volatility, and oxidative stability qualities are needed. Branched alkanes from hydrocracking of long-chain *n*-paraffins are a dependable base oil component that gives lubricants these characteristics. Many advancements have been made in producing these alkanes, such as aldol condensation of acetone with furans along with total hydrodeoxygenation to produce C8-C15 alkanes and two molecules of furfural undergoing benzoin condensation [11], farnesene derivatization or others.

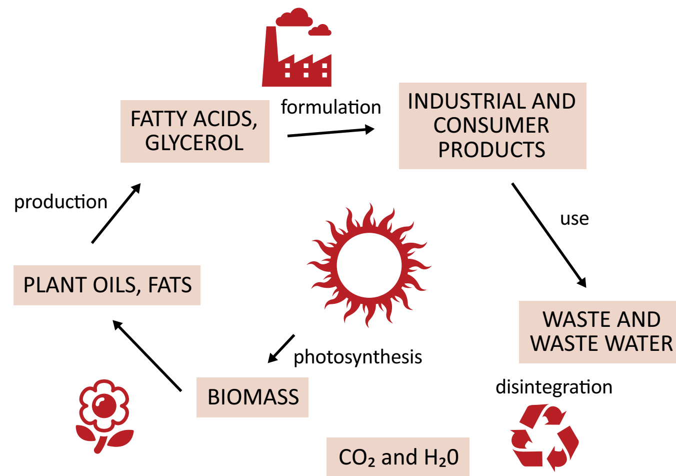

FIG. 1. Use cycle of renewable resource-based products [7]

In a 2017 study, it was found that branched alkanes can be produced from renewable biomass furfural and acetone. Figure 2 demonstrates the process involving the aldol condensation of furfural with acetone, hydrogenation of resultant C_{13} ketone, and condensation of the ketone with furfural to create C_{23}. Finally, the hydrodeoxygenation of C_{23} forms branched C_{23} alkanes. The entire process gives an overall 50.6% yield.

Impressive advancements have been made in the use of vegetable oils in lubrication and hydraulic oils, including different types of vegetable and crop seeds being used to further preserve the environment. Likewise, advancements in the methods of producing branched alkanes from biomass have allowed for renewable lubricants to be made.

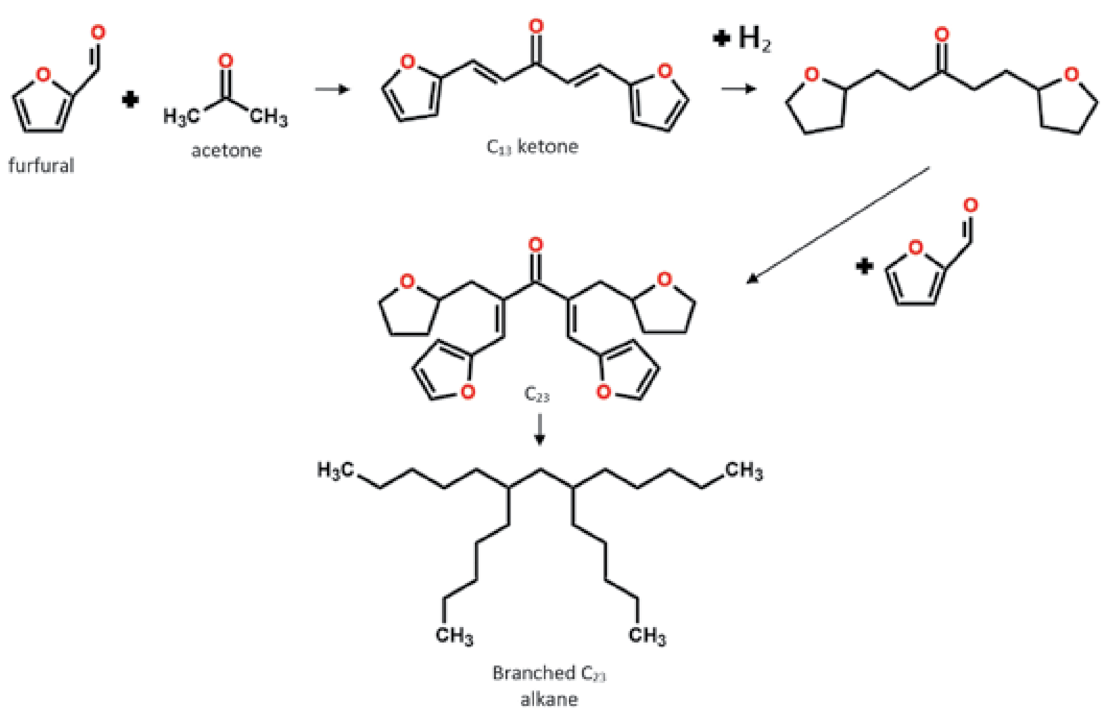

FIG. 2. Branched C_{23} synthesis from acetone and furfural through a four-step process

TABLE 2. Properties of two gear oils, FLENI and FLENDER, with and without 5 wt% ILs [14]

Gear oils + ionic liquids	Density (g/cm³)* at 15°C	Viscosity (mm²/s) at 40°C*	Viscosity (mm²/s) at 100°C*	Viscosity index
FLENI	0.900	305.90 (270.67)	23.40 (19.878)	96
+ 5% [BMP][NTf_2]	0.912	317.59 (291.28)	24.58 (21.223)	99
+ 5% [Choline][NTf_2]	0.915	320.06 (288.05)	24.92 (21.529)	100
FLENDER	0.860	323.38 (273.42)	35.20 (28.50)	154
+ 5% [BMP][NTf_2]	0.870	334.50 (290.17)	36.22 (30.68)	155
+ 5% [Choline][NTf_2]	0.915	342.68 (293.75)	38.79 (31.68)	164

* Measured in a SVM 3000 Stabinger viscometer (ASTM D7042, 2270)

The branched alkanes give renewable lubricants several superior characteristics compared to their mineral-oil-based lubricant counterparts, and biodegradable fluids can also be used in other oils and fluids due to their characteristics and capabilities.

STEAM TURBINE OILS

Steam turbine oils are used for bearing lubrication in machinery and typically last between 5 and 10 years [12]. The visco-temperature characteristics of turbine oil dictate the performance quality of the lubricant when in contact with components, such as a sliding bearing. There are currently two visco-temperature characteristics models, the Reynolds and Vogel models. In both models, dynamic viscosity decreases as temperature increases [13], causing concern when using lubricants in systems that constantly experience high temperatures.

Many lubricating fluids are composed of mineral oil. The oxidation of mineral oil in these types of lubricants causes viscosity to increase. Additives, such as oxidation and rust inhibitors and extreme pressure additives, are often added to lubricants to increase quality performance. Ionic liquids (ILs) have become more widely used and accepted as having good lubricating properties due to their suitability for many applications and high thermal stability. Furthermore, many ILs are more environmentally friendly and more readily form tribofilms [14]. Tribofilms are produced when ILs tribochemically react with the surface they are lubricating during rubbing contact, resulting in a protective layer, or film produced at the lubricating interface [15].

Table 2 shows increased viscosity values when the ILs were added to the gear oils. FLENI is a mineral-based oil and FLENDER is a polyalphaolefin-based oil, with both being used as wind turbine gearbox lubricants. The 5–6.5% increase of viscosity at 100C for FLENI and the 2.9–10.2% increase of viscosity at the same temperature for FLENDER demonstrates that the presence of ILs has a beneficial effect on turbine oils and their viscometric properties.

In a 2019 study, three different ILs were synthesized through a process beginning with imidazolium cation synthesis, followed by conversion to benzotriazole bearing imidazolium cation, and finally exchanging anions to form the ILs. The oxidative stability of ISO VG 32 base oil, IRGALUBE 2030A, and the three ILs was tested according to the ASTM D2272 standard. The RPVOT ASTM D2272 is conducted at 150°C under pressurized oxygen [4]. The ISO VG 32 base oil, a virgin base oil without any additives, had a pressure drop time of 100 minutes. The addition of 0.5 wt% of IRGALUBE 2030A, a turbine oil additive for long-term service with corrosion inhibitors and antioxidants, had a time of 180 minutes. Finally, the addition of 0.5 wt% of the three ILs was >300 minutes. The synthesized ILs containing BF_4^-, PF_6^-, and other non-toxic and safe compounds demonstrated a significantly greater oxidative resistance compared to the readily available IRGALUBE additive [16]. Further research of IL as lubricant constituents might lead to significant advancements.

HYDRAULIC FLUIDS

Because hydraulic fluids can leak, toxic materials that can damage the environment should be avoided. Bioderived biodegradable fluids made of triglycerides demonstrate good lubrication properties due to the presence of polar ester groups and long fatty acid chains. Molecular films form from the polarity of these fatty moieties, giving these lubricants their characteristic oiliness [17]. The concept of biodegradability also corresponds with high-performance quality in hydraulic components, such as oxidation and thermal stability, and wear protection of the fluids [18].

The compressibility of a hydraulic lubricant can affect dynamic performance [9]. The density-pressure characteristics of vegetable oils used as hydraulic fluids must be observed to determine compressibility characteristics of a biodegradable counterpart of mineral oil. The ester functional group in vegetable oils provides dipole intermolecular forces, resulting in greater molecular packing. The greater molecular packing directly corresponds to higher density values compared to mineral oil because mineral oils do not have this functional group present. Higher density values were found to be correlated with lower carry-over, higher heat-transfer coefficient, and greater oil separation efficiency.

The ageing of fluids is an inevitable process that can affect fluid characteristics, as oxidation and hydrolysis can directly result in changes in the stability and performance quality of the fluids. Figure 3 (page 28) provides an overview of the mechanisms of ageing and the direct results of these mechanisms

The change in biodegradability of bioderived hydraulic fluids made of synthetic esters can also demonstrate that ageing

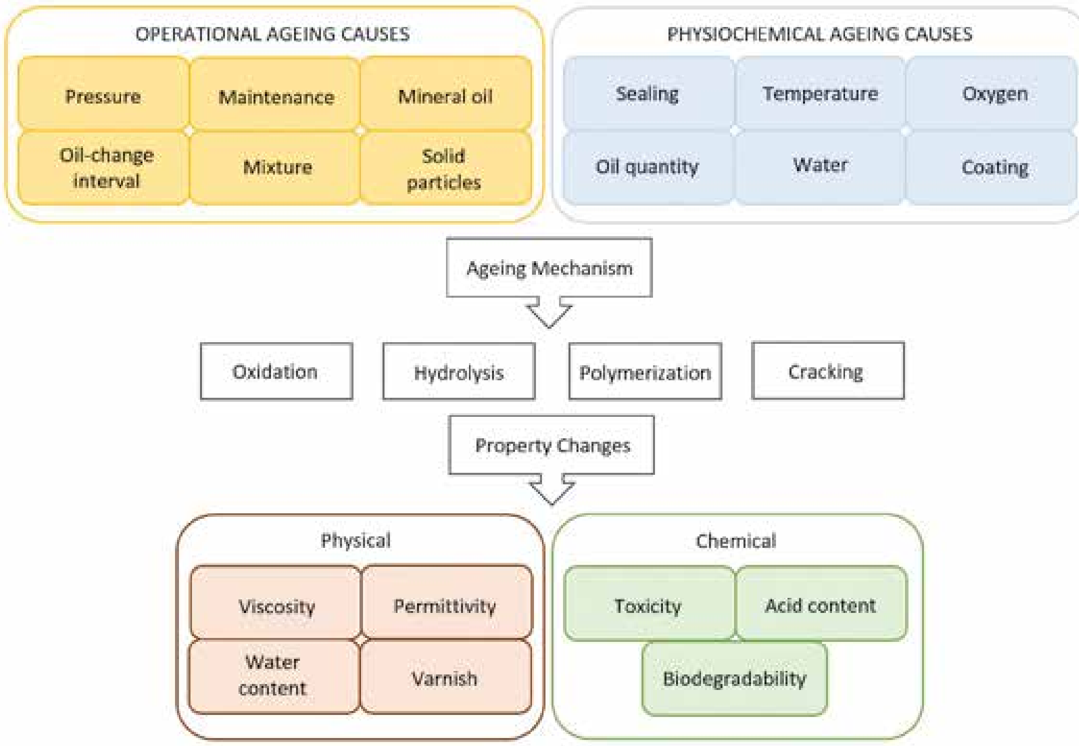

FIG. 3. Ageing process of hydraulic fluids and the resulting effects on fluid properties [18]

has occurred. When a bioderived hydraulic fluid that is 60% readily biodegradable according to OECD standards is mixed with mineral oil, its biodegradability percentage decreases between 10 and 12%. The hydraulic fluid had a kinematic viscosity of approximately 35mm^2/s and was made of synthetic esters with ISO 15380 HEES specifications. The decrease in biodegradability implies that mineral oil should not be used in junction with ester-based oils because this significantly reduces the environmentally friendly impact that biodegradable fluids possess.

TRANSFORMER OILS

Transformer units use fluids with insulation and coolant properties, with mineral oil being the most common transformer fluid with these properties. As a transformer oil, mineral oil is difficult to clean when leaked and is oxidatively unstable. The polynuclear aromatic hydrocarbons in mineral oil can be released into the environment if a transformer explodes, with these hydrocarbons being harmful to people and the environment [19].

The oil crisis of the 1970s introduced a need for renewable transformer fluids to be used in place of mineral oil. Vegetable oils with low polyunsaturation are good alternatives to mineral oils because of their biodegradability and environmentally safe qualities [20]. The water content of transformer insulating oil increases over time and can weaken dielectric properties. It has been determined that the water content of vegetable insulating oil was less than that of mineral insulating oil during the same period by analysis of IEC 60814. The higher hygro-

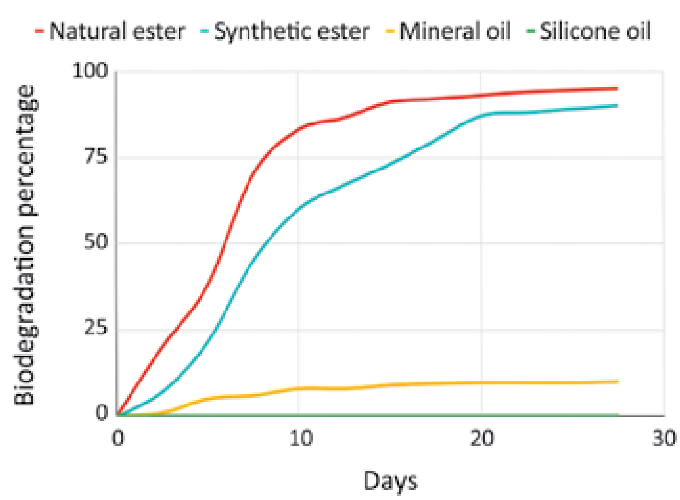

FIG. 4. Biodegradabilities of four different kinds of oil [22]

scopicity of esters is greater than that of mineral oil and allows the esters to form hydrogen bonds, accounting for the lower water content in vegetable oil, thus demonstrating better performance.

Palm fatty acid ester (PFAE) is a biodegradable transformer oil with higher oxidative stability compared to mineral oil and natural esters [21]. As a transformer oil, the presence of an esteryl group in PFAE allows for hydrogen bonding, corresponding with a great water affinity. This provides better protection of transformer cellulose insulation compared to mineral oil that does not have this esteryl functional group present. PFAEs, like vegetable oils, have high biodegradability properties with low polyunsaturation. PFAE has a significantly greater biodegradation percentage than mineral oil, with a biodegradability of 77%, which is comparable to the best esters in Figure 4.

The biodegradation percentages of the four oils were measured over 28 days using the OECD 301 regulation guideline. Natural and synthetic esters demonstrated a substantially higher biodegradation percentage over the same time compared to mineral and silicone oil. These results conclude that esters impose less harm on the environment compared to oils composed of non-biodegradable components, while also providing longer activity as a transformer oil.

It can be expected that in the coming years, biodegradable fluids will continue to be used in several applications because of their noteworthy efficiency and characteristics as these types of oils and lubricants. An increase in the lubricant market share is also expected as more experimentation and implementation are completed.

Raj Shah is a director at Koehler Instrument Company in New York, where he has worked for the last 25 years. He is a peer-elected Fellow of IChemE, STLE, AIC, NLGI, INSTMC, CMI, The Energy Institute, and The Royal Society of Chemistry. Shah has a Ph.D in Chemical Engineering from the Pennsylvania State University and is a Fellow from the Chartered Management Institute, London; a Chartered Scientist with the Science Council, UK; a Chartered Petroleum Engineer with the Energy Institute; and a Chartered Engineer with the Engineering council, UK. An ASTM Eagle award recipient, he recently coedited the bestseller, Fuels and Lubricants Handbook*, details of which are available at https://www.astm.org/DIGITAL_LIBRARY/MNL/SOURCE_PAGES/MNL37-2ND_foreword.pdf.*

A 2020 recipient of the illustrious Tau Beta Pi eminent engineer title, Shah is an active volunteer and on advisory board of directors at several US universities. He is a member of the editorial advisory committee for Inform magazine and has over 300 publications in numerous journals. More information on Raj can be found at https://www.che.psu.edu/news-archive/2018/Alumni-Spotlight-Raj-Shah.aspx. He can be reached at rshah@koehlerinstrument.com.

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The authors would like to thank long-term AOCS member Svajus Asadauskas for his helpful edits to this article.

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Targeted pest control using biotechnology

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

Rebecca Guenard

More and more gene therapies are being commercialized to fight human disease. Scientists have identified the gene responsible for the most common cause of childhood brain cancer and the gene that produces misshapen red blood cells in sickle cell disease patients. More importantly, they have discovered how to switch these gene off using synthetic small molecules as drug therapies. Several clinical trials are underway, and eventually gene therapies may eradicate these life-threatening, genetic diseases.

Just as researchers picked through the genomes of humans and other mammals, looking for evolutionary clues and disease inducing errors, they also evaluated the genomes of plants and insects. Like the treatments that have been discovered as possible therapies for human disease, switching off the genes of pests has become a likely method for ridding agriculture of devastating invasions. A recent publication in the journal *Cell* shows how controlling one gene in the whitefly (a crop pest) could lead to a new kind of pesticide that selectively eliminates harmful insects (https://doi.org/10.1016/j.cell.2021.02.014).

"My colleagues in Beijing were specifically looking for genes in whiteflies that could help them neutralize plant toxins," says Ted Turlings. "That is how they stumbled on this particular gene." Turlings, a chemical ecology professor at the University of Neuchâtel in Neuchâtel, Switzerland, collaborated with a team of researchers from the Chinese Academy of Agricultural Sciences in Beijing, China, to identify the *BtPMaT1* gene which allows the pests to tolerate a plant compound meant to kill them.

Plants and insects have battled for co-existence for over 400 million years. In that time, plants have established biochemical defenses to withstand an insect attack. They produce abundant secondary metabolites called phenolic glycosides that contribute to a plant's bitter flavors and pharmaceutical activities. These phenolic compounds are derived from salicyl alcohols and formed through glycosylation or esterification.

Plants presumably invested their metabolic resources into synthesizing these compounds to conquer herbivorous insect invaders, but the insects never surrendered. Some insects actually sequester phenolic glycosides and use them in their own defensive arsenal. In response, plants have developed rare glycosides through unique synthesis or produce a combination of several different compounds.

However, these efforts do not always prevail. The whitefly, for example, can neutralize toxic phenolic glycoside compounds—a trick it likely learned from the plants it infested for millions of years.

With the recent pandemic, we are all familiar with viruses and how they enter a cell, find its genome, merge with its genes, and replicate in the host. In the process, they leave behind their genetic material. The human genome is riddled with remnants of ancient viruses. In fact, many genes represent the spoils of war, won after a virus was defeated and then used to the host's advantage. This is likely also the case for the *BtPMaT1* gene discovered by the Chinese team.

"They compared whole genomes in the databases and they did not find this gene in any other insect except in three closely related whitefly species," says Turlings. "They did find similar genes in plants. That was the first indication that the gene actually came from plants at some point." He says, based on the phylogeny of the insect, this horizontal gene transfer from plants occurred more than 30 million years ago. It must have since become a crucial part of the crop pest's proliferation, but now researchers can categorize it as a weakness.

The *BtPMaT1* gene attaches a malonyl group to some phenolic glucosides, disarming the compounds as a threat to the insect (Fig.1). Because of this gene, whiteflies can invade fields of crops and feed on their leaves without being harmed by the toxins they contain. However, researchers found they could block the whiteflies' defense by feeding them a specific sequence of genes that switch off the flies' detoxifying abilities.

RNA interference (RNAi) is a mechanism used to silence a gene by introducing synthetic double-stranded RNA (dsRNA)

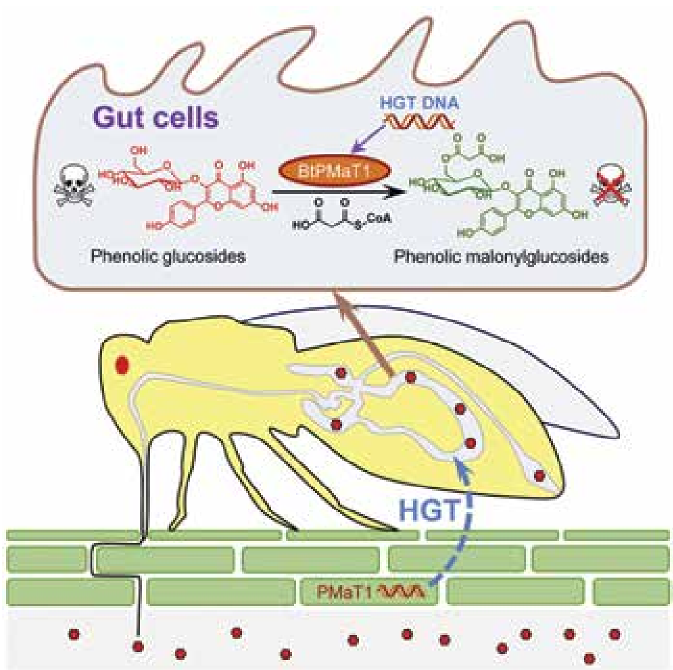

FIG. 1. Researchers have identified a gene which allows whiteflies to neutralize toxic phenolic glycosides by attaching a malonyl group as the molecules pass through their gut. The researchers confirmed they can kill whiteflies by genetically modifying a plant to contain DNA that switches off that gene. Source: Xia, J., *et al.*, *Cell, 184*, 7, 1693-1705.E17, 2021.

into cells. Plants use this process naturally as a form of protection from viruses and other foreign genetic material. It is part of their immune response that prevents the self-propagation of an invading species. Plant cells trigger the immune response when they encounter external dsRNA, which enzymes then clip into smaller segments. After a series of steps, complementary interference RNAs stop transcription of the genes in the segments, silencing their expression. Made-man dsRNA, introduced by researchers, induces the same effect.

Turlings says, among other experiments, his collaborators genetically manipulated tomato plants to produce a dsRNA that interferes with the *BtPMaT1* gene function when the whiteflies ingested the leaves' phloem sap. "Almost all of the whiteflies died," he says. "It was extremely effective in controlling the whiteflies and had no effect on the other insects that were feeding on these plants."

This potential to specifically target damage-causing insects while leaving beneficial ones unharmed has led scientists and start-ups to determine how they might use RNAi as a means of pest control. Insecticide resistance is a growing agricultural concern due to the widespread use of chemical pesticides. Concurrently, consumers are more aware of the environmental risks and health issues many of these chemicals inflict, favoring products they consider safer.

The first commercial RNAi product was developed by Monsanto before Bayer CropScience acquired the company. The seed, trade named SmartStax Pro, is a transgenic product designed to protect against corn rootworm. The product was approved in the United States in 2017, and has cleared regulatory hurdles in China and Canada. It will be ready for distribution in 2022 (https://tinyurl.com/smartstaxRNAiseed).

Aside from equipping plants with an internal pesticide, researchers have been considering other delivery methods like viruses and sprays. A virus designed with a genome containing a specific debilitating sequence could be released to infect and replicate in unwanted insects, where it would produce dsRNA molecules directly in their cells. Sprays represent a more conventional means of introducing the insecticide, where insects can acquire dsRNA after feeding on a treated plant.

Several problems must be addressed before this kind of technology can be widely used in agricultural pest control. Primarily, most European Union countries do not currently allow farmers to grow this type of genetically modified crop. Beyond that, genetic material cannot survive long enough in ambient conditions to be sprayed onto crops. Like the mRNA in COVID-19 vaccines, dsRNA would need to be protected by encapsulation in lipid nanoparticles. Even then it would have to endure a range of environmental conditions before reaching an insect's digestive system, where it would have to stay intact long enough to be absorbed into its cells. Finally, releasing a genetically modified virus into the wild introduces a slew of additional concerns. Viruses adapt quickly and could subvert the efforts of RNAi or cause more agricultural problems than they cure.

Still, the idea of just switching off a gene to alleviate a major agricultural woe is enticing. Through their observation of epigenetics, scientists understand that sometimes all it takes is a methyl group to silence gene expression in subsequent generations. Commercializing such a technology to eliminate crop pests is admittedly more complicated than current gene therapy strategies using synthetic molecules to silence genes that cause human disease. Crop scientists are not just correcting a coding error, they are attempting to kill insects by reprograming millions of years of evolution. However, the ability to use genetics for targeted pest control is in its infancy, and as scientists decipher how to harness its potential valuable agricultural advancements are likely to follow.

Rebecca Guenard is the associate editor of Inform *at AOCS. She can be contacted at rebecca.guenard@aocs.org.*

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European Commission to reopen cosmetics regulation under chemicals strategy

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

The European Commission will revise the cosmetics regulation to implement the targets of the EU chemicals strategy and aims to release a legislative proposal by the end of 2022, an official has confirmed.

The raft of updates, including changing the regulation's scope to address environmental endpoints for the first time, is a blow to industry, which had expressed fears that the text would be reopened along with REACH after the strategy's publication.

Roberto Scazzola, a policy officer at DG Grow, told delegates at *Chemical Watch*'s Key Regulatory Updates conference on March 22, 2021, that the Commission is likely to release a roadmap, or "inception impact assessment", within weeks. A full impact assessment may follow in the second half of the year.

Scazzola said some upcoming changes to the cosmetics regulation will be subject to the codecision procedure, which involves votes in the European Parliament and Council and is used for "fundamental changes".

They will include an action to address environmental endpoints—a ban on persistent, bioaccumulative, and toxic (PBT) chemicals.

As the legal text currently only covers human health endpoints, the move could set a precedent for including further environmental actions in future.

Scazzola said "changes will have to be made" to the legislation to include the new environmental endpoints, and that it is "too early to know" but he "would not exclude" the possibility of future environmental measures under the regulation. Future actions will depend on subsequent changes to the CLP Regulation, he added.

The Commission also intends to move the work of its Scientific Committee on Consumer Safety (SCCS), which currently evaluates the safety of cosmetics ingredients, to an EU agency, with a proposal expected in 2022.

Industry had previously signaled its concern that the regulation would be reopened after the strategy was published last year, saying it could lead to "potential overkill" with "no ingredients left to put in products".

The Commission has launched several working groups to implement various parts of the strategy. The stakeholder working group on cosmetics will meet two to three times a year, and Scazzola said that industry will be briefed on upcoming changes and have the opportunity to give feedback on the roadmap and future impact assessment.

In addition to actions on ingredients, such as per- and polyfluoroalkyl substances (PFASs), under the strategy, cosmetic products will also be subject to specific actions on consumer goods, including:

- a ban on endocrine disruptors (EDCs) with exemptions for "essential" use;
- a ban on PBT chemicals;
- a potential ban on immunotoxic and neurotoxic chemicals and those toxic to specific organs;
- extending generic risk management to ingredients in consumer products; and
- provisions on combination effects.

The Commission expects to publish proposals for these changes by the end of 2022 and undertake a review of the regulation's definition of nanomaterials by the end of 2021.

Meet **Sanja Natali**

Member Spotlight is a slice of life that helps AOCS members get to know each other on a more personal level.

(Clockwise from the left) Sanja Natali, daughter Mia (age 10), husband Joao, and daughter Ada (age 5).

Fast facts

Name	Sanja Natali
Joined AOCS	2018
Education	Ph.D. in chemical engineering from New York University (New York, New York, USA)
Job title	Customer Application Development, Performance Liquid Technology
Employer	ExxonMobil Chemical Co. (Houston, Texas, USA)
Current AOCS involvement	Session chair at the AOCS Annual Meeting & Expo, associate editor of the *Journal of Surfactants and Detergents*, treasurer/secretary of the Surfactants and Detergents Division

PROFESSIONAL

Flash back to when you were 10 years old. What did you want to be when you grew up?
I wanted to be a pilot as I always had the desire to travel and explore the world. I'm from Serbia, but my parents got married in Japan and traveled to India and Thailand afterward. In addition, my father worked in Austria when I was young, and we spent every summer in Greece, so I was always fascinated by different countries and cultures.

Why did you decide to do the work you are doing now?
I started my industrial career as a rheologist, but soon afterward I was introduced to the amazing world of surfactants by Samuel Rosen Memorial Award-recipient and now dear friend, Charles Hammond. I was fascinated by the strongly nonlinear behavior of surfactants and the need to understand the fundamental science behind this behavior to use them to their maximum capacity.

Is there an achievement or contribution you are most proud of? Why?
In a previous job, two brilliant scientists from India worked on one of the projects I led, although we never met in person. Last year, after speaking at a surfactant conference in India, one of the two scientists came to talk with me. What made it special was his words about how intellectually excited he was working on that project and how people around him even noticed that. I am very passionate about my work, and what makes me really proud is when I can inspire and coach other people to share the same passion.

What event, person, or life experience has had the most influence on the direction of your life?
My mother. She always believed in me and was a great role model. She was very scientifically minded, progressive, and a career-driven woman. Sadly, she passed away quite young, but the confidence that she had that I would do great things in life inspired me to dare and explore different paths.

PERSONAL

How do you relax after a hard day of work?
By enjoying time with my family. We always have dinner together and discuss interesting topics, from art and politics to science. Sometimes, that results in experiments that we need to conduct, which add extra fun. Currently, we are working on a still-motion animation movie about two birds who travel to the moon.

What is the most impressive thing you know how to do?
I would say that the most *unexpected* thing I know how to do is decorating food. I enjoy making picture food art with my daughters' lunches. I hope this is teaching them a valuable lesson on the importance of devoting time to things that you like, even if the end product is not meant to last.

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$1,000 honorarium and a plaque

IOP Division ACI/NBB Glycerine Innovation

Recognizes outstanding achievement for research in new applications for glycerine with emphasis on commercial viability. Sponsored by the American Cleaning Institute (ACI) and the National Biodiesel Board (NBB).

$5,000 honorarium and a plaque

PCP Division Lifetime Achievement Award

Recognizes significant contributions to the advancement of protein and co-products through research and applications.

$1,500 travel allowance and a plaque

Nominations

PRO Division Distinguished Service

Recognizes and honors outstanding and meritorious service to the oilseed processing industry.

$1,000 travel allowance and a certificate

S&D Division Samuel Rosen Memorial

Recognizes a surfactant chemist for significant advancement or application of surfactant chemistry principles. Initiated by Milton Rosen and this Division.

Plaque

S&D Division Distinguished Service

Recognizes outstanding and commendable service to the surfactants, detergents and soaps industry.

Plaque

Student Awards

NOMINATION DEADLINE ▶ OCTOBER 1, 2021

Honored Student

Recognizes graduate students in any area of fats and lipids. To receive the award, a candidate must remain a registered graduate student and must not have received a graduate degree or have begun career employment before the Society's Annual Meeting.

$500 travel allowance for U.S. and Canada residents [$1,000 travel allowance for recipients residing outside of those countries], complimentary AOCS Annual Meeting registration and lodging, and a certificate

Hans Kaunitz

Recognizes a student conducting research related to fats, oils and detergent technology.

$1,000 honorarium, $500 travel allowance and a certificate

Lipid Chemistry and Nutrition

Recognizes outstanding performance and achievement of a graduate student conducting research in lipid chemistry and nutrition. Sponsored by Seawit Co., Inc.

$1,000 honorarium, $550 travel allowance and a plaque

Lipid Processing and Biotechnology

Recognizes outstanding performance and achievement of a graduate student conducting research in lipid processing and biotechnology. Sponsored by Myande Group Co., Inc.

$1,000 honorarium, $550 travel allowance and a plaque

Ralph H. Potts Memorial Fellowship

Recognizes a graduate student conducting research related to fatty acids and their derivatives, such as long-chain alcohols, amines and other nitrogen compounds. Sponsored by Nouryon.

$2,000 honorarium, $500 travel allowance and a plaque

AOCS Division Student Awards

Recognizes over 20 students from any institution of higher learning, who are studying and doing research towards an advanced degree in fats, oils and related materials.

Awards range from $50 to $1,000 and a certificate

Each award has its own specific and unique nomination requirements. Please refer to the website for full details.

The award recipient must agree to attend the AOCS Annual Meeting & Expo and present an award lecture. The 2022 AOCS Annual Meeting will be held in Atlanta, Georgia, USA, from May 1–4, 2022.

Major challenges and budding opportunities for antimicrobial coatings

Markets in Motion covers market trends, opportunities, developments, and future prospects in AOCS-related industries.

Hrishikesh Kadam

Exponential spread of the coronavirus outbreak and its impact, particularly on the construction sector, was a major roadblock for the antimicrobial coatings industry during 2020. Due to supply chain disruptions and lack of funds, many projects remained in unfinished stages, while the completion timelines for numerous new projects were pushed forward.

For instance, in March 2020, the US State of Washington issued a shutdown order for ongoing residential and commercial projects, since construction is not considered to be an essential activity. Numerous major airport construction projects worldwide were halted or postponed the following June due to concerns about reduced air travel (https://tinyurl.com/4ncdnypx).

Meanwhile, the pandemic has drastically changed consumer perceptions about hygiene and cleanliness. This has drawn attention to antimicrobial coatings as an important safety measure, leading to their widespread application in public, residential, and commercial spaces.

During February 2021, the Leeds-based British supermarket chain Asda Stores Limited collaborated with shop equipment provider Wanzl to introduce trolley handles and in-store surfaces treated with antimicrobial coatings, including the Addmaster Biomaster coating formulated by Shield Master. The antimicrobial technology has been successfully tested to ISO standards against the coronavirus SARS-COV-2, and the protection lasts for the intended lifetime of the product.

During the same month, Everbrite Coatings launched the CrobialCoat antimicrobial technology designed specifically for keeping highly polished or matte metals, hard plastics, or hardwoods clean. The coating can be applied in both residential and commercial environments such as homes, schools, hospitals, restaurants, and other spaces.

Plano-based company Allied BioScience recently announced plans to double its capacity after witnessing rapid growth in national distribution of its antimicrobial coatings during the pandemic (https://tinyurl.com/rtvvu2). In May 2020, Allied BioScience funded a research study conducted by researchers at the University of Arizona (UA) which tested a coating designed by the company to specifically act against viruses.

The study found that just a single application of the coating can keep surfaces clear of the coronavirus for up to three months. The researchers observed that post application, the amount of virus on coated surfaces was reduced by nearly 90% in just 10 minutes and by 99.9% in about two hours. The coating works by attacking the virus' protective fat layer and denaturing proteins present in it, effectively twisting them out of shape. Although it is no substitute for regular cleaning, it could be an effective solution in between regular disinfection and sanitization.

TECHNOLOGICAL ADVANCES AND GROWING USE OF ANTIMICROBIAL COATINGS IN NEW AREAS

Mounting health and personal hygiene concerns are constantly driving new innovations in the development of antimicrobial coatings, creating a positive outlook in new applications such as aerospace, packaging, and many more. Currently, a team of astronauts aboard the International Space Station (ISS) are experimenting with an antimicrobial coating developed by Boeing and The University of Queensland, designed to fight bacteria and viruses (https://www.dailymail.co.uk/sciencetech/article-9263795/Antimicrobial-coating-designed-Boeing-kill-coronavirus-tested-astronauts.html).

With new applications of high-performance functional antimicrobial coatings continuously emerging, the global antimicrobial coatings market size is projected to surpass an annual valuation of over US$6.3 billion by 2026 (https://www.gminsights.com/industry-analysis/antimicrobial-coatings-market-report).

With the rise in online shopping during the pandemic, San Francisco-based Designsake Studio announced the launch of its new Matter technology to manufacture a novel form of silver antimicrobial protective coating that works with a range of packaging materials.

The Matter antimicrobial technology has been certified by the US Food and Drug Administration and US Environmental Protection Agency and provides effective protection against 99% of the microbes. It can be applied to shipping boxes and other packaging materials as well as other materials such as plastics, paper, metal, glass, and textiles.

As new applications of antimicrobial coatings continue to emerge, standardization, evaluation of antimicrobial properties, and stability will become increasingly important, especially for long-term applications. The next generation of antimicrobial coating formulations is expected to be multifunctional, which can integrate multiple antimicrobial actions.

Hrishikesh Kadam is a graduate in electronics and telecommunication engineering who has always found writing fascinating. Driven by a never-ending passion for content creation and experience in writing personal blogs, Hrishikesh blends his technical knowledge and expertise to write articles across various domains.

PATENTS

Combination of baclofen, acamprosate, and medium-chain triglycerides for the treatment of neurological disorders

Cohen, D., *et al.*, Pharnext, US10905672, February 2, 2021

The present invention relates to combinations and methods for the treatment of neurological disorders related to amyloid beta toxicity and/or neuronal death and/or glucose-impaired neuronal metabolism. More specifically, the present invention relates to novel combinatorial therapies of Alzheimer's disease, Alzheimer's disease-related disorders, frontotemporal dementia, Parkinson's disease, Lewy body dementia, Huntington's disease, peripheral neuropathies, alcoholism or alcohol withdrawal, neurological manifestations of drug abuse or drug abuse withdrawal, amyotrophic lateral sclerosis, multiple sclerosis, spinal cord injury, epilepsy, traumatic brain injury or brain ischemic events based on baclofen, acamprosate, and at least one medium-chain triglyceride.

Methods for predicting drug responsiveness in cancer patients

Knudsen, S., Oncology Venture ApS, US10907214, February 2, 2021

The present invention features methods, devices, and kits for detecting a level of one or more biomarkers in a patient having cancer or determining the responsiveness of a patient having cancer to a treatment, such as treatment with a secretory phospholipase A.sub.2 (sPLA.sub.2) hydrolysable, cisplatin-containing liposome. The invention further includes methods of treating a patient having cancer by administering, e.g., the liposome.

Biotechnological production of omega-functionalized carboxylic acids and esters thereof

Schaffer, S., *et al.*, Evonik Operations GmbH, US10913960, February 9, 2021

A microbial cell, which is genetically modified to increase the expression relative to the corresponding genetically unmodified cell of an AlkB alkane hydroxylase (E.sub.b) having an amino acid sequence at least 95% identical with the amino acid sequence of SEQ ID NO: 1 and a wax-ester synthase (E.sub.f) having an amino acid sequence at least 95% identical with the amino acid sequence of SEQ ID NO: 2. The cell does not have a genetic modification that increases formation of a carboxylic acid or a carboxylate ester from a simple carbon source.

Trans-free and low-saturated-fat cocoa butter alternative

Serna, C. and Fernanda, A., Team Foods Colombia S.A., US10918115, February 16, 2021

A cocoa butter alternative and the method of making thereof that includes 62–84% saturated fatty acid content having 20–40% lauric acid content, 8–20% myristic acid content, 9–37% palmitic acid content, and 3–17% stearic acid content. The fat may include 16–38% unsaturated fatty acid content, including 15–30% oleic acid content; 10% linoleic acid content and 4% linolenic acid content; and 28–95% of interesterified fat mixture of lauric and non-lauric vegetable oils. The fat mixture may include 40–60% of palm kernel oil, coconut oil, or fractions thereof and 40–60% of palm oil or fractions. The fat may include 2–40% of vegetable oil such as sunflower, safflower, low-erucic rapeseed/canola, soybean, high-oleic sunflower, high-oleic safflower, high-oleic rapeseed, high-oleic canola, high-oleic soybean, palm fractions, hybrid palm, or olive oils and 5–40% of lauric hard fat such as palm kernel or coconut oil or fractions thereof.

Compositions for dust control and methods making and using same

Kakadjian, S., *et al.*, Keane Group Holdings, LLC, and NexTier Completion Solutions Inc., US10920133, February 16, 2021

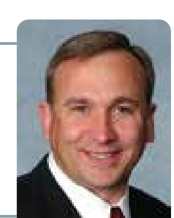
Proppant dust suppression compositions including: (a) at least one sugar alcohol ester or a sugar alcohol esters or a plurality of sugar alcohol esters; or (b) a mixture of at least one glyceride or a glyceride or a plurality of glycerides and at least one sugar alcohol ester or a sugar alcohol esters or a plurality of sugar alcohol esters and methods for using the compositions, where the treated proppant composition has between about 30% and 100% proppant dust reduction and wherein the at least one sugar alcohol ester improves flowability of treated proppant so that the treated proppant has reduced screen out propensity.

Enzymatic enrichment of n-3 fatty acids in the form of glycerides

Basheer, S., *et al.*, Enzymocore Ltd., US10927391, February 23, 2021

Disclosed are various enzymatic processes for the enrichments of oils with omega-3 fatty acids, and specific lipase preparations for use with these processes.

Patent information was compiled by Scott Bloomer, a registered US patent agent and Director, Technical Services at AOCS. Contact him at scott.bloomer@aocs.org.



A conversation with the new Editor-in-Chief of *JAOCS*

In May 2021, Silvana Martini became the first female Editor-in-Chief (EIC) of the *Journal of the American Oil Chemists' Society* (*JAOCS*), AOCS' flagship journal for original scientific research and technological advances on fats, oils, oilseed proteins, and related materials.

Martini is a professor in the Department of Nutrition, Dietetics, and Food Sciences at Utah State University, Logan, USA, where she studies the physicochemical and sensorial characterization of lipids and other food materials and how the quality of these materials is affected by their nano-, micro-, and macroscopic structure. She pioneered the use of ultrasound to change the physical properties of fats and directs the Aggie Chocolate Factory at Utah State University, where students in the school's food science program gain real world experience by making and selling chocolates. Her work has been recognized by awards, including the AOCS Timothy L. Mounts Award in 2019, and the American Chemical Society's Young Scientist Award—Agricultural and Food Chemistry Division in 2014.

JAOCS' new EIC is a familiar face within AOCS. In addition to making a significant impact as a senior associate editor for *JAOCS*, she is an AOCS fellow and member of the AOCS Governing Board. In the following conversation, Martini discussed her goals for the journal.

HOW DID YOUR PREVIOUS ROLE AS A SENIOR ASSOCIATE EDITOR PREPARE YOU FOR THIS NEW ROLE?

As an associate editor and senior associate editor, I became familiar with the great diversity of studies published in the journal, especially with those topics that are not directly related to my area of expertise. It is amazing to see such a broad spectrum of areas covered by *JAOCS* and the excellent scientific papers that are published by researchers around the world. Publication of high-quality papers is only possible given the dedication and commitment of the editorial board and many reviewers worldwide.

INCREASING THE NUMBER AND QUALITY OF SUBMISSIONS IS A KEY GOAL FOR THE JOURNAL. HAVE YOU GIVEN SOME THOUGHT TO HOW THIS MIGHT BE ACCOMPLISHED?

Yes, I have some ideas on how to increase the number and quality of submissions. I would like to increase *JAOCS*' presence in social media to promote the journal, its outstanding papers, and encourage new submissions. In collaboration with editorial board members, we are working on various special issues and review articles. We believe that all these activities will increase submissions, readership, and citations of the papers published in *JAOCS*.

WHAT OTHER GOALS MIGHT YOU HAVE FOR THE JOURNAL?

My primary goal is to increase the impact factor of the journal. I know this is not an easy task, but I am confident that working as a team with the Editorial Board we will be able to accomplish this.

THEME ISSUES ARE VERY POPULAR AND GENERATE SIGNIFICANT INTEREST FOR JOURNALS. DO YOU HAVE PLANS TO EXPLORE OPPORTUNITIES ALONG THESE LINES?

Yes, we are working on two special issues right now. We are hoping to have these published in 2022.

WHAT ARE THE BENEFITS OF PUBLISHING WITH A JOURNAL THAT COVERS A BROAD RANGE OF RESEARCH AREAS (LIKE *JAOCS*) INSTEAD OF A JOURNAL THAT FOCUSES ON A SPECIFIC RESEARCH AREA (LIKE THE *JOURNAL OF SURFACTANTS AND DETERGENTS*)?

In my opinion, the main benefit of publishing in a journal like *JAOCS* is that it reaches a wider range of readership. Researchers can benefit from having access to a wide array of topics outside their area of expertise.

EXTRACTS & DISTILLATES

The full version of all AOCS journal articles are available online to members at www.aocs.org/journal. This column builds on that member benefit by primarily highlighting articles from other journals.

ANA Analytical	BIO Biotechnology
EAT Edible Applications	LOQ Lipid Oxidation and Quality
H&N Health and Nutrition	IOP Industrial Oil Products
PRO Processing	PCP Protein and Co-Products
S&D Surfactants and Detergents	

Review Articles

H&N New perspective toward nutritional support for malnourished cancer patients: role of lipids

Wang, Y., *et al.*, *Compr. Rev. Food Sci. Food Saf. 20*: 1381–1421, March 2021, https://doi.org/10.1111/1541-4337.12706.

Nutritional support has become an essential part of multidisciplinary comprehensive treatment for cancer. Lipids are essential nutrient source for the human body, and in clinical practices, it has a positive interventional effect on cancer patients. However, the contribution of lipids in nutritional support of cancer patients is still poorly understood. Moreover, the sensory and physicochemical properties of lipids can severely restrict their applications in lipid-rich formula foods. This article summarizes the existing studies related to the associations—and possible mechanisms—of different lipids and improved malnutrition in cancer patients. Challenges and effective solutions for processing lipids into formula foods are discussed, and a novel method for treating malnutrition, including developing individualized lipid nutrition for different patients based on their genotype and enterotype, is proposed.

Original Articles

ANA Quantitative determination of peroxide value of edible oil by algorithm-assisted liquid interfacial surface-enhanced Raman spectroscopy

Jiang, Y., *et al.*, *Food Chem. 344*: 128709, May 2021, https://doi.org/10.1016/j.foodchem.2020.128709.

Edible oil is an indispensable food in daily life, but early detection of its lipid oxidation is difficult. Developing new, rapid, and accurate screening techniques is urgently needed for oil quality control. Here we developed a surface-enhanced Raman spectroscopy analyzer based on plasmonic metal liquid-like platform (PML-SERS) which could directly analyze the oil sample in ca. 3 min. This analyzer has the ability and sensitivity to identify fingerprint peak changes. Moreover, the relative Raman intensity, I1265/1436, has a good correlation with peroxide value (POV), which is used for quantitative detection. The fitting model combined with principal component analysis (PCA) realized rapid spectral recognition for determining POV in edible oil oxidation. The relative deviation between the POV measured by PML-SERS and the national standard method (NSM) was less than 10%. Our platform provided a practical solution for ultra-sensitive and fast analysis of POV in oil oxidation.

ANA IOP S&D A novel technique for interface analysis: behavior of sophorolipids biosurfactant obtained from *Meyerozyma* spp. MF138126 during low-salinity heavy-crude experiments

Akanji, L.T., *et al.*, *Fuel 297*: 120607, August 2021, https://doi.org/10.1016/j.fuel.2021.120607.

A novel technique for interface behavior and thermodynamic properties analyses of sophorolipids (SLs) biosurfactant obtained from *Meyerozyma* spp. MF138126 under high-pressure high-temperature (HPHT), for low-salinity heavy-crude experiments is presented. An experimental rig for production of biosurfactant and determination of interfacial tension (IFT) under HPHT is developed specifically for the purpose of this investigation. A reduction of a factor of seven and nine in IFT was obtained for experiments between brine and heavy-crude at temperatures of 45°C and 65°C, respectively. Furthermore, with increasing temperature, the degree of SLs adsorption at the interface increases leading to a total collapse in the profiles of the adsorption graphs. The minimum area per molecule of SLs monomers for different conditions suggested that the interface weakens occupying more surface area as the temperature increases. The degree of counter-ion binding for SLs is obtained to be 0.86. The computed Gibbs free energy of micellisation is –1940 KJ/mol; which is exergonic depicting favorable reaction and spontaneous in forward direction. At a fixed temperature of 25°C and pressure of 45 bar, IFT value of 0.251 mN/m was obtained. It is concluded that the produced SLs retained its molecular integrity and IFT reduction effectiveness under both unconfined and confined HPHT systems.

ANA IOP Comparative study of physicochemical and rheological property of waste cooking oil, castor oil, rubber seed oil, their methyl esters, and blends with mineral diesel fuel

Paul, A.K., *et al.*, *Mater. Sci. Technol. 4*: 148–155, 2021, https://doi.org/10.1016/j.mset.2021.03.004.

Physicochemical properties and rheological behavior of waste cooking oil (WCO), castor oil (CO), rubber seed oil (RSO), and their methyl esters (ME), as well as ME blends (5, 10 and 15 vol%) with diesel fuel were investigated. Rheological properties of samples were measured in the range of 25–80°C temperature and 5–300 s–1 shear rate. Similarly, rheological behavior of WCO, CO, and RSO based methyl esters (WCOME, COME, ROSME) and its blends (5, 10, and 15 vol%) with diesel fuel were also studied. Power law model was used to study the flow behavior of all the samples. The viscosity behavior of oils (WCO, CO and RSO), methyl esters (WCOME, COME and RSOME), and their blends with diesel fuel showed Newtonian nature in the temperature range of 25–80°C. The viscosity values of the chemically modified oil samples (via transesterification) were found to be lower than the original oil samples. However, WCO, CO and their methyl esters showed a slight deviation from Newtonian behavior between shear rate intervals of 5–100 s–1. The dynamic viscosity of RSO (25.58 mPa.s) was less than that of WCO (49.91 mPa.s) and CO (338.08 mPa.s). At 40°C, the kinematic viscosity values of RSOME (3.81 mm2/s) and WCOME (3.36 mm2/s) were lower than the value of COME (10.59 mm2/s). The dynamic viscosities of the samples were found to be dependent on fatty acids chain length, unsaturation, and temperature. According to fatty acid composition and physicochemical properties of the oils samples, WCO, CO, and RSO are suitable for substituting edible feedstock to make biodiesel production sustainable. The fuel properties of the methyl esters and their blends with diesel were estimated as per ASTM D6751 biodiesel standards.

BIO PCP S&D Valorization of biodiesel side stream waste glycerol for rhamnolipids production by *Pseudomonas aeruginosa* RS6

Baskaran, S.M., *et al.*, *Environ. Pollut. 276*: 116742, May 2021, https://doi.org/10.1016/j.envpol.2021.116742.

Biodiesel side stream waste glycerol was identified as a cheap carbon source for rhamnolipids (RLs) production which at the same time could improve the management of waste. The present study aimed to produce RLs by using *Pseudomonas aeruginosa* RS6 using waste glycerol as a substrate, and to evaluate their physico-chemicals properties. Fermentation conditions, such as temperature, initial medium pH, waste glycerol concentration, nitrogen sources, and concentrations resulted in different compositions of the mono- and di-RLs produced. The maximum RLs production of 2.73 g/L was obtained when *P. aeruginosa* RS6 was grown in a basal salt medium supplemented with 1% waste glycerol and 0.2 M sodium nitrate at 35°C and pH 6.5. At optimal fermentation conditions, the emulsification index (E_{24}) values of cooking oil, diesel oil, benzene, olive oil, petroleum, and kerosene were all above $E_{24=}50\%$. The surface tension reduction obtained from 72.13 mN/m to 29.4–30.4 mN/m was better than the surface activity of some chemical-based surfactants. The RLs produced possessed antimicrobial activities against gram-negative and gram-positive bacteria with values ranging from 37% to 77% of growth inhibition when 1 mg/mL of RLs was used. Concentrations of RLs below 1500 microgram/mL did not induce phytotoxicity effects on the tested seeds (*Vigna radiata*) compared to the chemical-based surfactant, SDS. Furthermore, RLs tested on zebrafish (*Danio rerio*) embryos only exhibited low acute toxicity with an LC_{50} value of 72.97 microgram/mL at 48 h of exposure, suggesting a green and eco-biochemical worthy of future applications to replace chemical-based surfactants.

EAT H&N PRO Lipids from algal biomass provide new (nonlamellar) nanovectors with high carrier potentiality for natural antioxidants

Clemente, I., *et al.*, *Eur. J. Pharm. Biopharm. 158*: 410–416, January 2021, https://doi.org/10.1016/j.ejpb.2020.11.013.

Lipid mesophases are lyotropic liquid crystalline systems which differ from liposomes and other globular aggregates in dilute regimes due to their inner ordering. It is known that natural lipids enable to obtain a rich variety of nanosystems and many of them have been proposed as delivery agents for bioactive compounds. Due to their packing parameters, several classes of lipids found in natural sources can self-assemble into nonlamellar structures. Among lipids occurring in plants and algae, triglycerides display this tendency. In this study, we examined new nanosystems built with lipids extracted from the marine microalga *Nannochloropsis* sp and their use as carriers for lipophilic antioxidants. The antioxidants studied, curcumin and tocopherol, were encapsulated with high rate in the carriers. The physico-chemical characterization of plain and loaded vectors showed their structure and localization site, as well as the structure-functionality relationship related to potential drug delivery. The results show that the cargo molecules play an active role in driving the interactions which characterize the overall structure of the aggregates. The systems studied showed several coexisting mesophases, the most predominant structure being of cubic symmetry.

EAT PRO Development of crackers with the addition of olive leaf flour (*Olea europaea* L.): chemical and sensory characterization

Faccioli, L.S., *et al.*, *LWT–Food Sci. Technol. 141*: 110848, April 2021, https://doi.org/10.1016/j.lwt.2021.110848.

Olive leaves (OL) are by-products of olive cultivation that are usually discarded, but due to the presence of bioactive compounds beneficial to health, they could be used. Thus, the objective of this paper is to develop a cracker from an olive leaf flour (OLF) and to verify the sensory effect of its use. Crackers were made from 5 formulations: F0 (without OLF), F3 (1,7 g/100 g), F5 (2,8 g/100 g), F7 (4 g/100 g), and F9 (5,1 g/100 g). In addition to OLF, the crackers had refined, whole wheat, and almond flour. Oleuropein quantification, macronutrients, and sensory analysis were performed using Quantitative Descriptive Analysis (QDA), as well as consumer acceptance and preference, in addition to purchase intent. The amount of oleuropein found in the cookies was 1.30 mg/g to 1.80 mg/g. The addition of OLF does not change the macronutrients composition of the crackers. However, in the analysis of oleuropein, F9 showed a higher concentration of such compound ($p < 0.05$). The QDA showed significant difference among the formulations in the flavor attributes of herbaceous, and salty and bitterness taste, and in the green color ($p < 0.05$). In the Acceptability Index, F3 showed 83% acceptance, followed by F0 with 80%, F5 with 78%, F7 with 75%, and F9 with 71%. Crackers enriched with OLF, especially F3, are nutritious alternatives for consumption that have good acceptance by consumers.

EAT H&N Food by-products valorization: grape pomace and olive pomace (pâté) as sources of phenolic compounds and fiber for enrichment of tagliatelle pasta

Balli, D., *et al.*, *Food Chem. 355*: 129642, April 2021, https://doi.org/10.1016/j.foodchem.2021.129642.

Wine- and olive-oil-making by-products are rich sources of bioactive compounds suitable for fortifying staple foods. In this study, the profile of pasta (tagliatelle) fortified with 7% of grape pomace (GP) or olive pomace (pâté, OP) was studied, focusing on phenolic compounds after cooking. The enriched tagliatelle retained the same monoglycosylated and acetylated anthocyanins found in grape pomace. The fortified tagliatelle with a new milling by-product called pâté retained hydroxytyrosol after cooking (6.6 mg/100 g). In both types of enriched tagliatelle, the fiber content increased by approximately 3%, while the added phenols retained after cooking by tagliatelle fortified with GP and OP were 6.21 mg/100 g and 9 mg/100 g, respectively. The fortified tagliatelle retained good cooking resistance and texture after cooking, thus enhancing the nutritional profile of pasta, a staple food usually characterized by a negligible amount of phenolic compounds and fiber.

EAT H&N Technological quality and sensory acceptability of nutritive bars produced with Brazil nut and baru almond coproducts

Silva Lima, D., *et al.*, *LWT–Food Sci. Technol. 137*: 110467, April 2021, https://doi.org/10.1016/j.lwt.2020.110467.

The intake of almonds and nuts demonstrates benefits to human health due to their bioactive compounds. In Brazil, baru almonds and Brazil nuts are largely explored in communities through cooperatives. The objective of the present work was to develop and evaluate a nutritive bar with Brazil nut (BN) and baru almond (BA) by-products at concentrations of 0, 25, 50, 75, and 100% in formulations. Baru almonds showed higher protein content (24.95 g/100 g) than Brazil nuts (14.74 g/100 g), while Brazil nuts showed higher lipidic content (59.36 g/100 g). All the nutritive bar formulations could be classified as high mineral content, mainly iron, calcium, phosphorus, zinc, and magnesium. The firmness (instrumental texture) was the highest for BA100 (217.9 N), while the adhesiveness was the lowest (-23.62 N). The highest acceptability indexes for taste and texture (59 and 67%, respectively) were observed for BN25:BA75 while BA100 achieved the highest acceptability index for odor, color, and global perception

(71, 73, and 72%, respectively). Therefore, BN25:BA75 could be the most suitable formulation to be produced as it had a good nutritional content balance and obtained higher acceptance and preference in the sensory evaluation.

EAT The whole beast: consumers' perceptions of and willingness-to-eat animal by-products

Bearth, A., *et al.*, *Food Qual. Prefer. 89*: 104144, April 2021, https://doi.org/10.1016/j.foodqual.2020.104144.

Satisfying the global demand for proteins and avoiding food waste are global challenges. Promoting the consumption of animal by-products might contribute to the solution. The goal of our study was to investigate the role that different factors play for consumers' willingness to engage with animal by-products. For this, an online survey and experiment with consumers was conducted (N = 260). While food disgust sensitivity works as a barrier, social norms and culinary-based drivers increase people's willingness to engage with animal by-products. To expand consumer interest, measures could focus on increasing familiarity and reducing negative expectations regarding the sensory qualities of the product.

PRO EAT IOP BIO Intensified synthesis of palm olein designer lipids using sonication

Jadhav, H.B., *et al.*, *Ultrason. Sonochem. 73*: 105478, May 2021, https://doi.org/10.1016/j.ultsonch.2021.105478.

This study looked at intensified synthesis of designer lipids with application of ultrasound based on biocatalyzed reaction between long-chain triglyceride and medium-chain fatty acid. The effects of various reaction conditions like molar ratio of reactant, reaction temperature, and enzyme loading along with the effect of ultrasound parameters such as duty cycle and irradiation time on the rate of formation of designer lipids have been investigated. The ultrasound-assisted process was also compared with the traditional process to clearly bring out the intensification effects. During the study, it was clearly demonstrated that the optimum reaction conditions for maximum yield of designer lipids as 92% was molar ratio of medium chain fatty acid to long chain triglyceride as 4:1, reaction temperature of 40°C, enzyme loading of 3%, duty cycle of 70%, 240 W as power dissipation, and 360 min as reaction time. The recyclability study of enzyme showed its effectiveness up to 10 cycles. The synthesized designer lipid showed higher oxidative stability for 35 days and also showed Newtonian behavior with eye-appealing color. The study demonstrates development of an eco-friendly technique for intensified synthesis of designer lipids having numerous nutraceutical benefits.

PRO A novel deodorization method of edible oil by using ethanol steam at low temperature

Yang, C., *et al.*, *J. Food Sci. 86*: 394–403, January 2021, https://doi.org/10.1111/1750-3841.15578.

A novel deodorization method of edible oil by using ethanol steam at low temperature was developed. We compared the chemical changes in pre-deodorized rapeseed oil after anhydrous ethanol steam distillation at low temperature (140 to 220°C) (L-ESD) and conventional high-temperature (250°C) water-steam distillation (H-WSD) in terms of odor characteristics, physicochemical properties, micronutrient contents, antioxidant performance, and fatty acid composition. Compared with H-WSD (250°C for 60 min), L-ESD at 180°C for 80 to 100 min resulted in lower response values of electronic nose, free fatty acid (0.03% to 0.07%), and peroxide value (0.00 to 0.67 meq/kg), but higher retention of tocopherols (554.93 to 551.59 mg/kg), total phenols (43.36 to 45.42 mgGAE/kg), total carotenoids (65.78 to 67.85 mg/kg), phytosterols (585.80 to 596.53 mg/100 g), polyunsaturated fatty acids (27.95 to 28.01%), and better antioxidant properties. In conclusion, L-ESD can mitigate the damage of oil and thus significantly improve the safety of vegetable oils with a high retention of nutrients compared with conventional H-WSD.

PRO Environmental sustainability challenges of China's edible vegetable oil industry: from farm to factory

Bai, Y., *et al.*, *Resour. Conserv. Recy. 170*: 105606, July 2021, https://doi.org/10.1016/j.resconrec.2021.105606.

With increasing consumer demand and only 31% self-sufficiency, how to mitigate the supply of edible vegetable oil in an environmentally sustainable manner is a tremendous challenge for China. This study comprehensively qualified the potential environmental impact from major edible vegetable oil production (i.e., soybean oil, rapeseed oil, and peanut oil) in China through the life cycle assessment method. Results show that rapeseed oil and peanut oil are environmentally friendly. More than 20% of environmental contamination could be avoided in 2025 by replacing further increase in soybean oil production with a mix of the other products. The key contribution analysis indicates that the agricultural phase is a significant source of environmental pollution due to excessive fertilizer production and irrigation water consumption. During the oil processing phases of soybean oil and peanut oil, steam production also contributed to considerable environmental impact. Therefore, applying new fertilizers, developing water-saving irrigation technologies, and optimizing the steam heat exchange net are suggested. Moreover, increasing the oil extraction rate through electrotechnical technology has great potential in reducing the environmental damage caused by oil-bearing crop planting. Based on the spatial discrepancy in the agricultural phase, advantageous planting regions (e.g., Anhui, Henan, Shandong, and Jiangsu) are references for the further planting structure adjustment. Meanwhile, optimizing the industry layout is recommended to ensure the sustainable development of China's edible vegetable oil industry.

PRO IOP Two-step methanolysis and ethanolysis of olive pomace oil using olive-pomace-based heterogeneous acid catalyst

Ayadi, M., *et al.*, *Fuel 296*: 120678, July 2021, https://doi.org/10.1016/j.fuel.2021.120678.

Olive pomace (OP) and olive pomace oil (OPO) are low-cost, non-edible by-products of olive oil processing. Converting OPO into biodiesel by (trans-)esterification and olive pomace into a heterogeneous acid catalyst by sulfonation with sulfuric acid could promote waste-to-energy actions. OPO has a high fatty acid content of 126.39 mgKOH/goil, which does not allow the use of base catalyst for biodiesel production. Homogeneous acid catalyst such as sulfuric acid could be used, however the wastewater should be neutralized and the catalyst could not be regenerated nor reused. The objective of this study was to use the OP to produce a heterogeneous acid catalyst that will be used in the esterification reaction of OPO to produce biodiesel.

OP was pyrolyzed, activated with steam, and sulfonated. Then OPO esterification was performed as at 60°C and 65°C for 5 h under agitation at 400 rpm using methanol and ethanol, respectively. The optimization of reaction was performed using a full factorial design by varying oil-to-methanol/ethanol molar ratio (1:3, 1:6, and 1:9) and catalyst loading (10 wt%, 15 wt%, and 20 wt%). The optimum esterification conditions were obtained at 1:9 oil-to-ethanol molar ratio and 20 wt% catalyst. Final products acidities reached 1.14 mgKOH/goil and 3.89 mgKOH/goil with methanol and ethanol, respectively. Work was then focused on ethanolysis, and a second step of homogeneous alkali-catalyzed transesterification was performed. FAEE yield registered 95.7% using the products of optimized first step. The physical and chemical properties of final product were measured and meet EN14214 requirements except for the glycerides contents which were slightly higher than the norm. The final product registered a viscosity of 3.38 mm2/s, a flash point of 168°C, and a Cold Filter Plugging Point of 14°C. Its Copper Strip Corrosion class (1a) meets EN14214. Solid catalyst was regenerated and reused up to 6 cycles before being mechanically degraded.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